

Chapter 6

Thermochemical Conversion Processes

6.1 Introduction to Thermochemical Conversion Processes

Thermochemical biomass conversion includes a number of possible routes to produce from the initial biorenewable feedstock useful fuels and chemicals. Biorenewable feedstocks can be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels. Thermochemical conversion processes include three subcategories: pyrolysis, gasification, and liquefaction. Figure 6.1 shows biomass thermal conversion processes. A variety of biomass resources can be used to convert to liquid, solid, and gaseous fuels with the help of some physical, thermochemical, biochemical, and biological conversion processes. Main biomass conversion processes are direct liquefaction, indirect liquefaction, physical extraction, thermochemical conversion, biochemical conversion, and electrochemical conversion. Figure 6.2 shows the types and classification of biomass conversion processes. The conver-

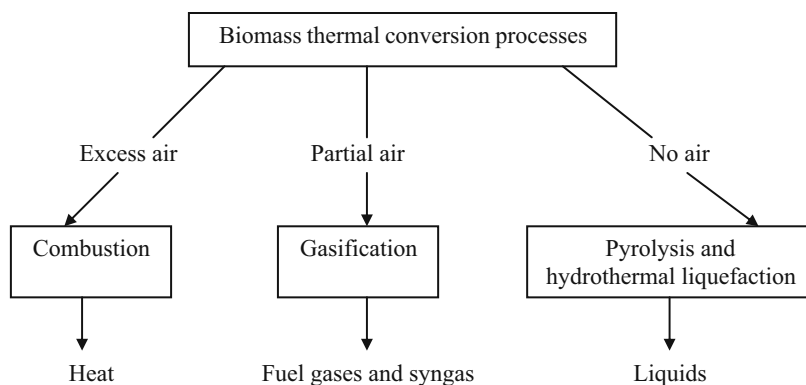


Fig. 6.1 Biomass thermal conversion processes

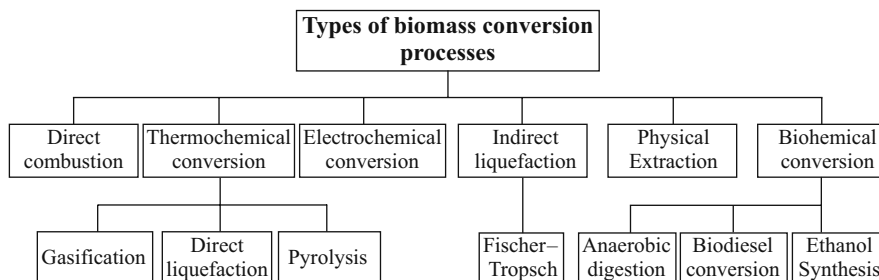


Fig. 6.2 Classification of biomass conversion processes

sion of biomass materials has the precise objective to transform a carbonaceous solid material, which is originally difficult to handle, bulky and of low energy concentration, into fuels having physico-chemical characteristics that permit economic storage and transferability through pumping systems.

Gasification of biomass for use in internal combustion engines for power generation provides an important alternate renewable energy resource. Gasification is partial combustion of biomass to produce gas and char at the first stage and subsequent reduction of the product gases, chiefly CO_2 and H_2O , by the charcoal into CO and H_2 . The process also generates some methane and other higher hydrocarbons depending on the design and operating conditions of the reactor.

Pyrolysis is the fundamental chemical reaction process that is the precursor of both gasification and combustion of solid fuels, and is simply defined as the chemical changes occurring when heat is applied to a material in the absence of oxygen. Flash pyrolysis of biomass is the thermochemical process that converts small dried biomass particles into a liquid fuel (biocrude) with a yield of almost 75%, and char and non-condensable gases by heating the biomass to 775 K in the absence of oxygen. Char in the vapor phase catalyzes secondary cracking. Figure 6.3 shows the bio-oil from flash pyrolysis of the biomass pyrolysis process.

Plasma arc and radio frequency (or microwave) heating refer to specific devices providing heat from electricity for gasification, pyrolysis, or combustion depending on the amount of reactive oxygen, hydrogen, steam, or other reactant



Fig. 6.3 Bio-oil from flash pyrolysis of biomass pyrolysis

fed to the reactor. Very high temperatures are created in the ionized plasma. Plasma arc processes use electricity passing through electrodes to produce a discharge converting the surrounding gas to an ionized gas or plasma. Gases heated in plasmas typically reach temperatures of 377 K and higher.

Thermochemical conversion (TCC) technologies were studied as early as the 17th century with the first patent issued in 1788 by Robert Gardner for his work in the gasification area. However, during the time span 1800–1970 TCC technologies were forgotten due to an abundance of oil. When TCC research continued, it began to focus on sources outside of wood and coal. TCC technologies include, but are not limited to, gasification, liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction. Gasification and liquefaction continue to be heavily researched and used commercially throughout the world. Researchers are focusing efforts to attempt to understand the complex reaction mechanisms that occur during these processes.

Thermochemical conversion is characterized by higher temperatures and conversion rates than most other processes. Thermochemical conversion includes a continuum of processes ranging from thermal decomposition in a primarily non-reactive environment (commonly called pyrolysis) to decomposition in a chemically reactive environment (usually called gasification if the products are primarily fuel gases). Pyrolysis can be considered an incomplete gasification process, in which a mixture of gaseous, liquid, and solid products is produced, each of which may have some immediate use to sustain the process. The characteristics of each of these processes can also vary depending on the oxidizing or reducing media, process temperature, and process pressure.

Two biomass conversion processes using water have been studied: hydrothermal upgrading (HTU) under subcritical water and supercritical water gasification (SCWG) in supercritical water conditions. For the design of the both biomass conversion processes, the following contributions of thermodynamics have been presented: phase behavior and phase equilibria in the reactor and separators, and an indication of favorable operation conditions and the trends in product distribution for the conversion reactions. A wide variety of fluids have been dealt with, from small molecules to large molecules, including non-polar and polar substances (Feng *et al.*, 2004).

HTU or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bio-products such as biocrudes. HTU is a thermochemical process for the conversion of wet biomass material under sub (near)-critical water conditions and produces a hydrophobic oil layer (biocrude), aqueous liquid products, gasses, and some solid remains. Biocrude is obtained in the yield of typically 40–50% and has reduced oxygen content (average 12%). The resulting bio-oil can be used for electricity production, but also upgraded into transportation fuel. The project involves the visualization of the process and the development of new reactors. SCWG provides a direct conversion of glucose to hydrogen, CO, CO₂ and CH₄ in water of 875 K and 30 MPa.

Processes relating to the liquefaction of biomass are based on the early research of Appell *et al.* (1971). These workers reported that a variety of biomass such as

Table 6.1 Comparison of liquefaction and pyrolysis

Process	Temperature (K)	Pressure (MPa)	Drying
Liquefaction	525–600	5–20	Unnecessary
Pyrolysis	650–800	0.1–0.5	Necessary

agricultural and civic wastes can be converted, partially, into a heavy oil-like product by reaction with water and carbon monoxide/hydrogen in the presence of sodium carbonate.

The pyrolysis and direct liquefaction with water processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst (Balat, 2008). At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Molten *et al.*, 1983). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are shown in Table 6.1.

6.2 Thermal Decomposition Mechanisms of Biorenewables

In previous studies, the mechanisms of thermal depolymerization of biomass were not extensively identified. Mechanisms have been poorly studied in the past due to difficulties in sampling the slurry during the process. These proposed reactions are general and the type of biomass will dictate the type of processes or reactions required to breakdown and rearrange molecules. The more complex the raw biomass is chemically, the more complex the reaction mechanisms required, and thus the increased difficulty in determining them.

The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. It was therefore to be expected that furan derivatives would readily be found among the decomposition products. The hemicelluloses decomposed more readily than cellulose during heating. The thermal degradation of hemicelluloses begins above 475 K.

Thermal degradation of cellulose proceeds through a gradual degradation, decomposition, and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The glucose chains in cellulose are first cleaved to glucose and, in a second stage, glucosan is formed by the splitting off of one molecule of water. Initial degradation reactions include depolymerization, hydrolysis, oxidation,

dehydration, and decarboxylation (Demirbas, 2000). Cellulose decomposes more readily than lignin by heating.

Lignin decomposes over a wider temperature range. As the residence time increases the quantity of unstable substances decrease. For example, quantitatively, 1-hydroxy-2-propanone and 1-hydroxy-2-butanone present high concentrations in the liquid products from fast pyrolysis. These two alcohols are partly esterified by acetic acid. In conventional slow pyrolysis, these two products are not found in so great a quantity because of their low stability (Beaumont, 1985; Demirbas, 2007). Many unstable fragments and radicals form from degradation of lignin. As a result, it is believed that as the reaction progresses the remaining mass becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases.

It is difficult to determine exactly what types of reactions occur during liquefaction processes. Liquefaction of carbonaceous materials takes place through a sequence of structural and chemical changes (Chornet and Overend, 1985; Demirbas, 2000).

The reaction mechanisms may not follow the exact order described above, and the reactions in biomass depolymerization process are much more complex. Many researchers have tried to investigate and propose reaction mechanisms, but no definitive study has been conducted.

A summary of some of the proposed mechanisms is given below. After “cracking” reactions a hydrolyzing of the polymers and monomers, such as glucose, are then further reduced with the presence of reductive compounds. The oxygen element is eliminated, and high hydrogen and carbon containing compounds are yielded. To increase the conversion rate of organic matter to oil, a high hydrogen content in the feedstock is desirable. The use of hydrogen gas has been studied by Datta and McAuliffe (1993) and Kranich (1984). No difference in yields between CO and H₂ used as a process gas were noted. Appell *et al.* (1980) concluded that the use of CO was more than efficient for conversion to oil products.

It has been stated that the water-gas shift reaction under high temperatures would be responsible for the increase in the conversion rate from organic matter to oil. He *et al.* (2008) determined that any process gas can produce bio-oil, and that the initial gas prevented complete vaporization of the slurry during processing. A water-gas shift reaction has been proposed to be responsible for the increase in the conversion rates of organic matter to oil (Appell *et al.*, 1980). According to the water-gas shift reaction, the hydrogen radicals then react with other oxygen containing functional groups to eliminate oxygen elements and yield hydrocarbon like compounds. Carbon monoxide, as a highly reductive compound, participates in the redox reactions directly. It combines with oxygen in the hydroxyl and carboxyl groups to form CO₂. The hydrogen radical that is released is then ready to combine with carbon. Carbon dioxide forms through numerous routes and can form through decarboxylation reactions as well.

It is difficult to determine exactly what types of reactions occur during liquefaction processes. Liquefaction of carbonaceous materials takes place through

a sequence of structural and chemical changes, which involve at least the following steps (Chornet and Overend, 1985; Demirbas, 2000).

1. Cracking and reduction of polymers such as lignin and lipids.
2. Hydrolysis of cellulose and hemicelluloses to glucose.
3. Hydrogenolysis in the presence of hydrogen.
4. Reduction of amino acids.
5. New molecular rearrangements through dehydration and decarboxylation.
6. Hydrogenation of functional groups.

The reaction mechanisms may not follow the exact order described above, and the reactions in biomass depolymerization process are much more complex. Many researchers have tried to investigate and propose reaction mechanisms, but no definitive study has been conducted.

The hydrogen radicals then react with other oxygen containing functional groups to eliminate oxygen elements and yield hydrocarbon like compounds. Carbon monoxide, as a highly reductive compound, participates in the redox reactions directly. It combines with oxygen in the hydroxyl and carboxyl groups to form CO₂. The hydrogen radical that is released is then ready to combine with carbon. Carbon dioxide forms through numerous routes and can form through decarboxylation reactions as well.

6.3 Hydrothermal Liquefaction of Biorenewable Feedstocks

Liquefaction was developed for coal conversion over a century ago. Liquefaction used for biomass conversions to bio-oils is grouped under the TCC area of energy conversion methods along with gasification and pyrolysis.

Liquefaction can be accomplished directly or indirectly. Direct liquefaction involves hydrothermal liquefaction and rapid pyrolysis to produce liquid tars and oils and/or condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products. The liquefaction of biomass has been investigated in the presence of solutions of alkalis (Eager *et al.*, 1982), propanol and butanol (Ogi and Yokoyama, 1993), and glycerine (Demirbas, 1985), or by direct liquefaction (Ogi *et al.*, 1985; Minowa *et al.*, 1994).

HTL or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bio-products such as biocrudes. A major problem with commercializing the HTL processes for biomass conversion today is that it remains uneconomical when compared to the costs of diesel or gasoline production. High transportation costs of large quantities of biomass increase production costs, and poor conversion efficiency coupled with a lack of understanding complex reaction mechanisms inhibits growth of the process commercially.

In the HTU process, biomass is reacted in liquid water at elevated temperature and pressure. The phase equilibria in the HTU process are very complicated due to

the presence of water, supercritical carbon dioxide, alcohols, as well as the so-called biocrude. The biocrude is a mixture with a wide molecular weight distribution and consists of various kinds of molecules. Biocrude contains 10–13% oxygen. The biocrude is upgraded by catalytic hydrodeoxygenation in a central facility.

Biomass, such as wood, with a lower energy density is converted to biocrude with a higher energy density, organic compounds including mainly alcohols and acids, gases mainly including CO₂. Water is also a byproduct. In the products, CO₂, the main component of the gas product, can be used to represent all gas produced, and methanol and ethanol represent organic compounds. In Table 6.2, the weight fraction of each component is assigned on the basis of the data of the vacuum flash of biocrude and the data of a pilot plant (Feng *et al.*, 2004). Figure 6.4 shows the block scheme of commercial HTU plant. The feedstocks, reaction conditions, and the products for the HTU process are given in Table 6.3.

Table 6.2 Representatives for the products from the HTU process

Product	Component	Weight fraction (%)
Biocrude	Polycarbonates	47.5
	Methyl- <i>n</i> -propyl ether	2.5
Gas	Carbon dioxide	25.0
Organic compounds	Methanol	5.0
	Ethanol	3.5
Water	Water	16.5

Table 6.3 Feedstocks, reaction conditions, and products for the HTU process

Biomass feedstocks	Wood and forest wastes
	Agricultural and domestic residues
	Municipal solid wastes
	Organic industrial residues
	Sewage sludge
Reaction conditions	Temperature: 300–350°C
	Pressure: 12–18 MPa
	Resistance time: 5–20 min
	Medium: liquid water
Main chemical reactions	Depolymerization
	Decarboxylation
	Dehydration
	Oxygen removed as CO ₂ and H ₂ O
	Hydrodeoxygenation
Products (%w on feedstock)	Hydrogenation
	Biocrude: 45
	Water soluble organics: 10
	Gas (>90% CO ₂): 25
Thermal efficiency	Process water: 20
	70–90%

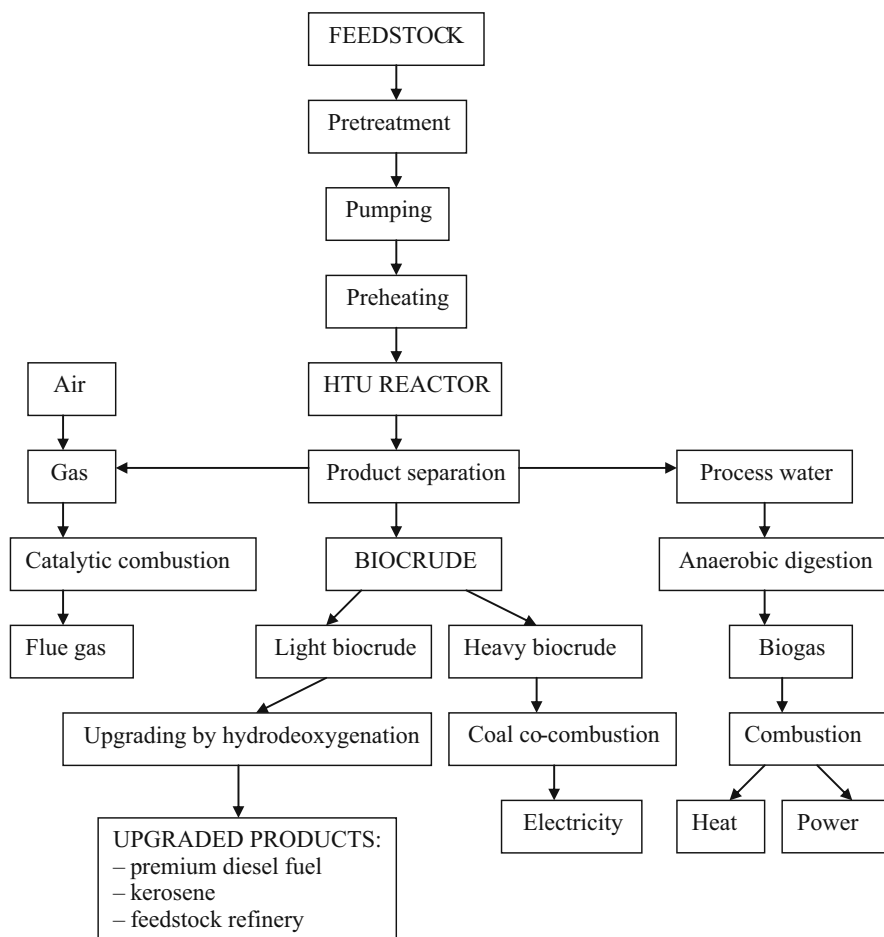


Fig. 6.4 Block scheme of a commercial HTU plant

One of the first HTL studies was conducted by Kranich (1984) using municipal waste materials (MSW) as a source to produce oil. Three different types of materials from a MSW plant were used: primary sewage sludge, settled digester sludge, and digester effluent. Using a magnetically stirred batch autoclave with a hydrogen-feed system, a slurry feed device, a pressure and temperature recorder, and a wet-test meter for measuring gas product, Kranich processed the waste sources. The feedstock was first dried then powdered. The wastes were also separated into different oil and water slurries and processed separately. Temperatures ranged from 570–720 K with pressures up to 14 MPa. Retention times also varied between 20–90 minutes. Hydrogen was used as the reducing gas with initial pressures up to 8.3 MPa. Three types of catalyst were studied: sodium carbonate, nickel carbonate, and sodium molybdate. The slurry feedstock was injected into the reactor through a pressurized injector, and the oil product was extracted by

pentane and toluene. Results showed that organic conversion rates varied from 45–99%, and oil production rates were reported from 35.0–63.3%. Gas products were found to contain H_2 , CO_2 , and C_1 – C_4 hydrocarbons. The experimental results showed no significant differences between the applications of the three different catalysts. Kranich recommended that the water slurry system was not feasible for scale-up, and considerations of a commercial scale process were confined to only the oil slurry system. It was also concluded that no further development work on hydroliquefaction of sewage sludge to oil was necessary. Kranich's recommendation did not hold, mainly due to increases in crude oil prices and the need to find new technologies for energy procurement, and thus many studies on liquefaction of sewage sludge have since been conducted. Research has indicated that liquefaction is a feasible method for the treatment of sewage sludge wastes and has a high oil producing potential (Suzuki *et al.*, 1986; Itoh *et al.*, 1994; Inoue *et al.*, 1997). Today, HTL research is still being conducted with sewage sludge; however, focus has shifted to include many varieties of biomass materials.

Several technologies have been developed to convert biomass into a liquid bio-fuel with a higher heating value, such as gasification, fast pyrolysis and the HTU. In the HTU, the biomass is treated during 5–20 min with water under subcritical conditions (575–625 K, 10–18 MPa) to give a heavy organic liquid (biocrude) with a heating value of 30–35 MJ/kg. During this process, the oxygen content of the organic material is reduced from about 40% to between 10% and 15%. The removed oxygen ends up in CO_2 , H_2O and CO . After 1.6 s at 320°C and 25 MPa, 47% conversion of cellulose in water was obtained yielding hydrolysis products (cellobiose, glucose, *etc.*, 44%) and decomposition products of glucose (erythrose, 1,6-anhydroglucose, 5-hydroxymethylfurfural, 3%). Furthermore, it has been shown that cellobiose decomposes *via* hydrolysis to glucose, and *via* pyrolysis to glycosylerythrose and glycosylglycolaldehyde, which are further hydrolyzed into glucose, erythrose, and glycolaldehyde. Hydrolysis refers to splitting up of the organic particles into smaller organic fragments in water. Hydrothermal decomposition also acts on the large organic molecules reducing them into smaller fragments, some of which dissolve in water.

In the HTU process, biomass chips are pressurized and digested at 200–250°C with recycled water from the process. Subsequently the digested mass is pressurized to 12–18 MPa and reacted in liquid water at 300–400°C for 5–15 min. Under these conditions decarboxylation and depolymerization take place and a biocrude is formed, which separates from the water phase. Part of the process water is recycled. Obviously, the process is very simple high efficiency.

Hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. The treatment of organic wastes by SCW reaction in a homogeneous phase undergoes that interface mass transfer limitations are avoided, and reaction efficiencies of 99.9% can be achieved at residence times lower than 1 min. Because of the distinctive characteristics of water described above, hydrothermal reaction is an effective method for the treatment of organic wastes. The reaction can be performed under subcritical or supercritical condi-

tions. It can also be classified into two broad categories: (a) oxidative, *i.e.*, involving the use of oxidants, and (b) non-oxidative, *i.e.*, excluding the use of oxidants.

The process at subcritical temperatures results in the production of abundant quantities of dissolved organic matter. The dissolved organic matter contains significant quantities of volatile fatty acids, especially acetic acid, which remains in the liquid phase and can be significantly removed at supercritical temperatures.

6.3.1 The Role of Water During the HTL Process

Most substrates are not soluble in water under normal conditions, but salvation can occur between the hydroxyl groups and water under high temperatures and pressures. Water is a medium for intermediate hydrolysis of cellulose and other high-molecular weight carbohydrates to water-soluble sugars. The primary reactions in the conversion to oil are likely to involve the formation of low-molecular weight, water soluble compounds such as glucose.

Alkaline catalysts are water soluble as well, facilitating their dispersion throughout the process vessel in a readily available form. Water is also used to mix reactants, and to diminish condensations to chars by diluting the reaction intermediates.

Water is a reactant at high temperatures. Hydrogen may be added to the substrate through the water-gas shift reactions, which consumes carbon monoxide from carbon dioxide and hydrogen.

6.3.2 HTU Applications

The conversions of biomass wastes into biocrude or hydrogen have been successfully performed by the HTU processes. The application of hydrothermal reaction is transfer from organic wastes to useful materials, such as liquid fuel, hydrogen, glucose, organic acid, *etc.*

Hydrothermal reaction is a prominent method for the treatment of organic wastes and has been attracting worldwide attention. During the process, various reactions such as oxidation, hydrolysis, dehydration, and thermal decomposition can be carried out energetically, so that the reaction can be successfully used for oxidizing organic wastes to CO₂ and other innocuous end products, as well as for conversion of organic wastes to fuels or useful materials, such as biocrude, hydrogen, glucose, lactic acid, acetic acid, amino acids, *etc.* (He *et al.*, 2008).

In the HTU process, biomass chips are pressurized and digested at 473–523 K with recycled water from the process. Subsequently the digested mass is pressurized to 12–18 MPa and reacted in liquid water at 573–673 K for 5–15 min. Under these conditions decarboxylation and depolymerization take place and a biocrude is formed, which separates from the water phase. Part of the process water is recycled. Obviously, the process is very simple with high efficiency (Zhong *et al.*, 2002).

Hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. The treatment of organic wastes by SCW reaction in a homogeneous phase undergoes that interface mass transfer limitations are avoided and reaction efficiencies of 99.9% can be achieved at residence times lower than 1 min (Tester and Cline, 1999). Because of the distinctive characteristics of water described above, hydrothermal reaction is an effective method for the treatment of organic wastes. The reaction can be performed under near-critical or supercritical conditions. It can also be classified into two broad categories (Shanableh and Jomaa, 1998): (a) oxidative, *i.e.*, involving the use of oxidants, and (b) non-oxidative, *i.e.*, excluding the use of oxidants.

The process at subcritical temperatures results in the production of abundant quantities of dissolved organic matter (Jomaa, 2001). The dissolved organic matter contains significant quantities of volatile fatty acids, especially acetic acid, which remains in the liquid phase and can be significantly removed at supercritical temperatures (Jomaa *et al.*, 2003).

6.4 Direct Combustion of Biomass

Direct combustion is the old way of using biomass. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bioenergy production.

Research on direct liquefaction has been widely studied in the past, especially in the late 1970s and early 1980s for the purpose of alternative energy production. The feedstocks mainly consisted of wood and municipal solid wastes (MSW). Many aspects of the process are still being studied: the type and condition of various feedstocks, the operating carrier media, and reducing reagents. More specifically, researchers are focusing on various operating conditions, such as pH, processing gas, temperature, pressure, catalyst, retention time, solid content, gas to volatile solid ratio, and solvents for extraction or processing. In addition to studying these conditions researchers are still focusing their efforts on understanding the complex reactions that occur during the process. Biomass is complex by nature and varies by location. Developing a process that will handle many biomass sources, and one that is flexible to handle variations of biomass, is desirable to increase the potential impact that the process may have. Economics currently limit large scale biomass liquefaction treatment facilities, and on-site treatment remains difficult and expensive. However, researchers continue to move forward with their studies, and many alternative organic feedstocks have been processed through this technology as a means of waste management, as well as renewable energy production.

Combustion is the oxidation of the fuel for the production of heat at elevated temperatures without generating commercially useful intermediate fuel gases, liquids, or solids. Combustion of MSW or other secondary materials is generally

referred to as incineration. Particle temperatures in heterogeneous (*e.g.*, unsteady reactions between solid and gas phases) combustion can differ from the surrounding gas temperatures, depending on radiation heat transfer conditions.

Combustion of solids involves the simultaneous processes of heat and mass transport, progressive pyrolysis, gasification, ignition, and burning, with no intermediate steps and with an unsteady, sometimes turbulent, fluid flow. Normally, combustion employs an excess of oxidizer to ensure maximum fuel conversion, but it can also occur under fuel-rich conditions.

Combustion is a basic chemical process that releases energy from a fuel and air mixture. For combustion to occur, fuel, oxygen, and heat must be present together. Combustion is the chemical reaction of a particular substance with oxygen. Combustion represents a chemical reaction, during which from certain matters other simple matters are produced, this is a combination of inflammable matter with oxygen of the air accompanied by heat release. The quantity of heat evolved when one mole of a hydrocarbon is burned to carbon dioxide and water is called the heat of combustion. Combustion to carbon dioxide and water is characteristic of organic compounds; under special conditions it is used to determine their carbon and hydrogen content. During combustion the combustible part of fuel is subdivided into volatile part and solid residue. During heating it evaporates together with a part of carbon in the form of hydrocarbons combustible gases and carbon monoxide release by thermal degradation of the fuel. Carbon monoxide is mainly formed the following reactions: (a) from reduction of CO_2 with unreacted C,



and (b) from degradation of carbonyl fragments ($-\text{CO}$) in the fuel molecules at 600–750 K temperature.

The combustion process is started by heating the fuel above its ignition temperature in the presence of oxygen or air. Under the influence of heat, the chemical bonds of the fuel are cleaved. If complete combustion occurs, the combustible elements (C, H and S) react with the oxygen content of the air to form CO_2 , H_2O and mainly SO_2 .

If not enough oxygen is present, or the fuel and air mixture is insufficient, then the burning gases are partially cooled below the ignition temperature and the combustion process stays incomplete. The flue gases then still contain combustible components, mainly carbon monoxide (CO), unburned carbon (C), and various hydrocarbons (C_xH_y).

The standard measure of the energy content of a fuel is its heating value (HV), sometimes called the calorific value or heat of combustion. In fact, there are multiple values for HV, depending on whether it measures the enthalpy of combustion (ΔH) or the internal energy of combustion (ΔU), and whether for a fuel containing hydrogen product water is accounted for in the vapor phase or the condensed (liquid) phase. With water in the vapor phase, the lower heating value (LHV) at constant pressure measures the enthalpy change due to combustion. The heating value is obtained by the complete combustion of a unit quantity of solid fuel in an oxygen-bomb colorimeter under carefully defined conditions. The gross

heat of combustion or higher heating value (GHC or HHV) is obtained by the oxygen-bomb calorimeter method as the latent heat of moisture in the combustion products is recovered.

6.4.1 Combustion Efficiency

In general, combustion efficiency as defined in flue gas analysis standards is simply reduced by the stack loss. Combustion efficiency is based on the flue gas temperature and inlet air temperature. Combustion efficiency calculations assume complete fuel combustion and are based on the three following factors: (1) the chemistry of the fuel, (2) the net temperature of the stack gases, and (3) the percentage of oxygen or CO_2 by volume after combustion.

Combustion efficiency relates to the part of the reactants that combine chemically. Combustion efficiency increases with increasing temperature of the reactants, the increasing time that the reactants are in contact, increasing vapor pressures, increasing surface areas, and increasing stored chemical energy.

Figure 6.5 shows a typical diagram for combustion efficiency. Without enough combustion air the combustion efficiency is low. The combustion efficiency increases with fuel/air ratio. The combustion efficiency is lower than maximum value in the stoichiometric fuel/air mixture. Figure 6.6 shows the typical combustion efficiency vs. excess of air for natural gas.

6.4.1.1 Combustion Efficiency of Biofuels

Ethanol is an oxygenated liquid fuel and its combustion heat is considerably lower than those of petroleum-based fuels. Its characteristics as a transportation fuel can be attributed to its chemical composition. The oxygen provides more efficient

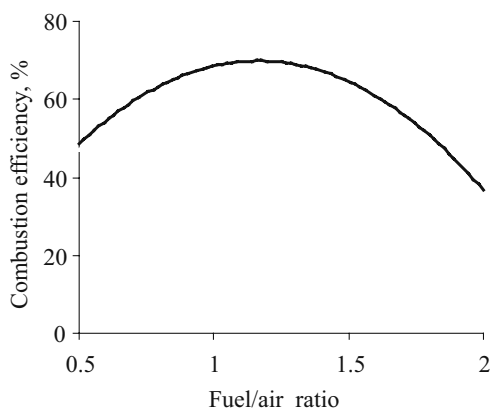
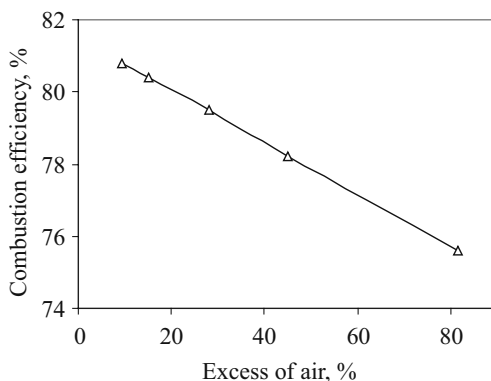


Fig. 6.5 A typical diagram for combustion efficiency

Fig. 6.6 Typical combustion efficiency values vs. excess of air for natural gas



combustion and cleaner emissions. At a stoichiometric air/fuel ratio of 9:1 in comparison with gasoline's 14.7:1, it is obvious that more ethanol is required to produce the chemically correct products of CO_2 and water. Ethanol has a higher octane number (108), broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time, and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine. The octane number of ethanol allows it to sustain significantly higher internal pressures than gasoline, before being subjected to predetonation. The disadvantages of ethanol include its lower energy density than gasoline, its corrosiveness, low flame luminosity, lower vapor pressure, miscibility with water, and toxicity to ecosystems.

Methyl alcohol has the lowest combustion energy of all engine fuels. However, it also has the lowest stoichiometric or chemically correct air-fuel ratio. Therefore, an engine burning methyl alcohol would produce the most power. It also is possible to take advantage of the higher octane number of methyl (114) alcohol and increase the engine compression ratio. This would increase the efficiency of converting the potential combustion energy to power. Finally, alcohols burn more completely, thus increasing combustion efficiency.

Biofuels, except biohydrogen, are oxygenated compounds. Oxygenates are just preused hydrocarbons having a structure that provides a reasonable antiknock value. Also, as they contain oxygen, fuel combustion is more efficient, reducing hydrocarbons in the exhaust gases. The only disadvantage is that oxygenated fuel has less energy content. For the same efficiency and power output, more fuel has to be burned.

The advantages of biofuels such as biodiesel, vegetable oil, bioethanol, bio-methanol, and biomass pyrolysis oil as engine fuel are liquid nature-portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, and biodegradability. Full combustion of a fuel requires in existence the amount of stoichiometric oxygen. However, the amount of stoichiometric oxygen generally is not enough for full combustion so as not to oxygenate the

fuel. The structural oxygen content of fuel increases combustion efficiency of the fuel due to an increase of the homogeneity of oxygen with the fuel during combustion. Because of this, the combustion efficiency and cetane numbers of vegetable oils and biodiesels are higher than diesel fuel; moreover the combustion efficiency of methanol/ethanol is higher than that of gasoline. The cetane number measures the readiness of a fuel to auto-ignite.

6.5 Direct Liquefaction

Liquefaction was developed for coal conversion over a century ago. Liquefaction used for biomass conversions to bio-oils is grouped under the TCC area of energy conversion methods along with gasification and pyrolysis. Liquefaction can be accomplished directly or indirectly. Direct liquefaction involves hydrothermal liquefaction and rapid pyrolysis to produce liquid tars and oils, and/or condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products.

Alkali salts, such as sodium carbonate and potassium carbonate, can act like the hydrolysis of cellulose and hemicelluloses, breaking them into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation. In the liquefaction process, the amount of solid residue increases in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 525 K, and that the radicals have a random tendency to form a solid residue through condensation or repolymerization.

The changes during the liquefaction process involve all kinds of processes such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis results in micellar-like substructures of the biomass. The depolymerization of biomass leads to smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups, and keto groups, also occur.

Due to the high moisture content and low heating value, biomass is not suitable to be used as energy directly. Aqueous liquefaction of lignocellulosic materials involves disaggregation followed by partial depolymerization of the constitutive families (hemicelluloses, cellulose and lignin). Wood, bark, and sugar cane bagasse have been directly liquefied by Ogi and Yokoyama (1993) under the same conditions. They observed that the yields of heavy oil were $50\% \pm 5\%$ for wood. As for bark, the yields of heavy oil ranged from 20–27%, which was much lower than those of the wood, while for sugar cane bagasse the yield was similar to those of wood.

Liquefaction of biomass and wastes is accomplished by natural, direct, and indirect thermal and fermentation methods. Natural liquefaction systems were the

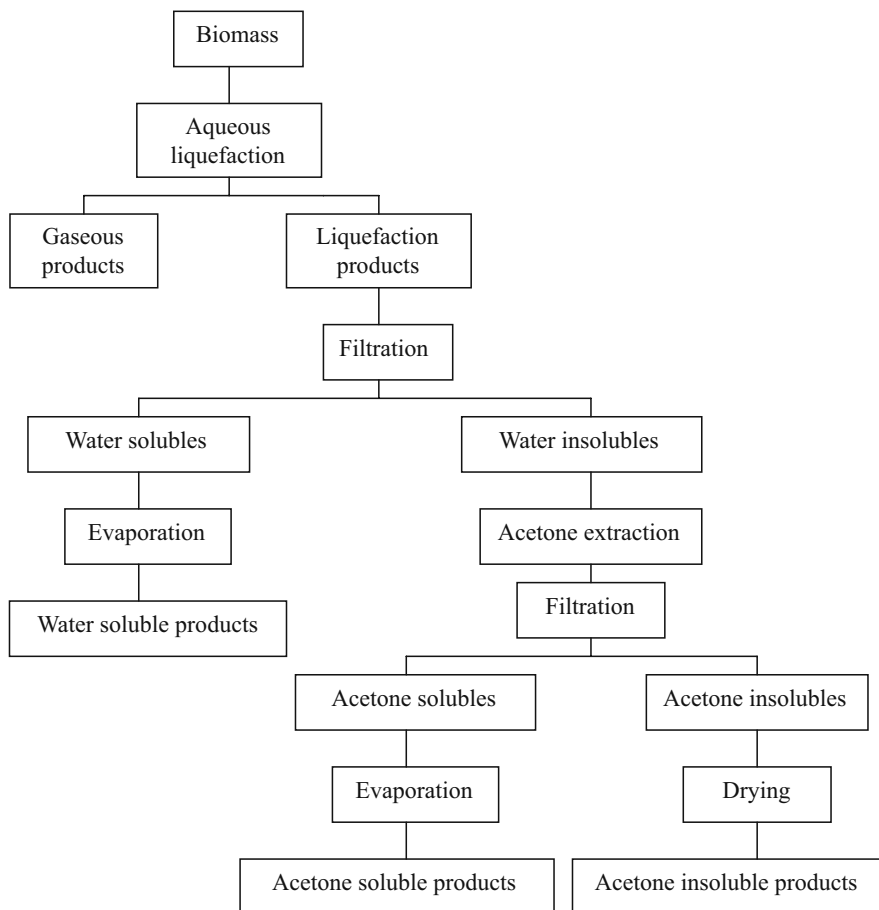


Fig. 6.7 Procedures for separation of aqueous liquefaction products

connection with certain arid-land plants and microalgae growth, and the resultant formation of lipids and hydrocarbons. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst.

Direct liquefaction of biomass by thermochemical means has been studied as a process for fuel production for the last 20 years. Direct liquefaction is either reaction of biomass components with smaller molecules such as H_2 and CO , or short-term pyrolytic treatment, sometimes in the presence of gases such as H_2 . Figure 6.7 shows the procedures for separation of aqueous liquefaction products

Indirect liquefaction involves successive production of an intermediate, such as synthesis gas or ethylene, and its chemical conversion to liquid fuels via Fischer-Tropsch processes.

6.6 Pyrolysis Processes

Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield can be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly (Mohan *et al.*, 2006). Pyrolysis has been used since the dawn of civilization. If some means is applied to collect the off-gasses (smoke), the process is called wood distillation. The ancient Egyptians practiced wood distillation by collecting tars and pyroligneous acid for use in their embalming industry. Pyrolysis of wood to produce charcoal was a major industry in the 1800s, supplying the fuel for the industrial revolution, until it was replaced by coal. In the late 19th century and early 20th century wood distillation was still profitable for producing the soluble tar, pitch, creosote oil, chemicals, and non-condensable gasses often used to heat boilers at the facility. The wood distillation industry declined in the 1930s due to the advent of the petrochemical industry and its lower priced products.

Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon rich gas mixture, an oil-like liquid, and a carbon rich solid residue. The products of pyrolysis can be gaseous, liquid, and/or solid. Flash pyrolysis describes the rapid, moderate temperature (67–875 K) pyrolysis that produces liquids. Biomass is heated at rates of 100–10,000 K/s, and the vapor residence time is normally less than 2 seconds. The oil products are maximized at the expense of char and gas.

Pyrolysis is a process similar to gasification except generally optimized for the production of fuel liquids (pyrolysis oils) that can be used straight or refined for higher quality uses such as engine fuels, chemicals, adhesives, and other products. Pyrolysis typically occurs at temperatures in the range of 675–975 K. Pyrolysis and combustion of pyrolysis-derived fuel liquids and gases also produce the same categories of end products as direct combustion of solids. Like gasification, their pollution control and conversion efficiencies may be improved.

Pyrolysis and direct liquefaction processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Demirbas, 2000). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase.

Fast pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production. Considerable efforts have been made to convert wood biomass to liquid fuels and chemicals since the oil crisis in the mid-1970s. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells, to energy crops such as sweet sorghum, sugar cane, sugar beet, saccharum, fiber sorghum, switchgrass, and miscanthus. The effect of pyrolysis reaction rate and the yield of the volatiles are the biomass composition and structure, heating rate, residence time, catalyst, and particle size. Although very fast and very slow pyrolyses of biomass produce markedly different products, the variety of heating rates, temperatures, residence times, and feedstock varieties found in the literature make generalizations difficult to define, in regard to trying to critically analyze the literature (Mohan *et al.*, 2006).

Catalytic cracking is a thermochemical process that employs catalysts using hydrogen-driven reducing reactions to accelerate the breakdown of high molecular weight compounds (*e.g.*, plastics) into smaller products for the purposes of improving selectivity and imparting certain desirable characteristics to the final product, such as volatility and flashpoint of liquid fuels. This cracking process is often employed in oil refinery operations to produce lower molecular weight hydrocarbon fuels from waste feedstocks. These include gasoline from heavier oils, distillation residuals, and waste plastic.

Rapid heating and rapid quenching produces intermediate pyrolysis liquid products, which condense before further reactions break down higher-molecular-weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher fast pyrolysis temperatures, the major product is gas. Many researchers have attempted to exploit the complex degradation mechanisms by conducting pyrolysis in unusual environments (Mohan *et al.*, 2006).

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better one. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (“gasification”), water (“steam gasification”), or hydrogen (“hydrogenation”). One of the most useful products is methane, which is a suitable fuel for electricity generation using high-efficiency gas turbines.

Cellulose and hemicelluloses form mainly volatile products on heating, due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments. The progressive increase in the pyrolysis temperature of wood leads to the release of volatiles thus forming a solid residue that is different chemically from the original starting material (Demirbas, 2000). Cellulose and hemicelluloses initially break into compounds of lower molecular weight. This forms an “activated cellulose”, which decomposes by two competitive reactions; one forming volatiles (anhydrosugars) and the other char and gases. The thermal degradation of the activated cellulose and hemicelluloses to form volatiles and char can be divided into categories depending on the

reaction temperature. Within a fire all these reactions take place concurrently and consecutively. Gaseous emissions are predominantly a product of pyrolytic cracking of the fuel. If flames are present, fire temperatures are high, and more oxygen is available from thermally induced convection.

Biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, such as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing. Among the liquid products, methanol is one of the most valuable products. The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase are higher than those of the non-aqueous phase. The point where the cost of producing energy from fossil fuels exceeds the cost of biomass fuels has been reached. With a few exceptions, energy from fossil fuels will cost more money than the same amount of energy supplied through biomass conversion.

The kinematic viscosity of pyrolysis oil varies from as low as 11 cSt to as high as 115 mm²/s (measured at 313 K) depending on the nature of the feedstock, the temperature of the pyrolysis process, the thermal degradation degree and catalytic cracking, the water content of the pyrolysis oil, the amount of light ends that have collected, and the pyrolysis process used. The pyrolysis oils have water contents of typically 15–30 wt% of the oil mass, which cannot be removed by conventional methods like distillation. Phase separation may partially occur above certain water contents. The water content of pyrolysis oils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, can lead to premature evaporation of the oil and resultant injection difficulties. The higher heating value (HHV) of pyrolysis oils is below 26 MJ/kg (compared to 42–45 MJ/kg for conventional petroleum fuel oils). In contrast to petroleum oils, which are non-polar and in which water is insoluble, biomass oils are highly polar and can readily absorb over 35% water (Demirbas, 2007).

The pyrolysis oil (bio-oil) from wood is typically a liquid, almost black through dark red brown. The density of the liquid is about 1200 kg/m³, which is higher than that of fuel oil and significantly higher than that of the original biomass. The bio-oils have a water contents of typically 14–33 wt.%, which cannot be removed by conventional methods like distillation. Phase separation may occur above a certain water content. The higher heating value (HHV) is below 27 MJ/kg (compared to 43–46 MJ/kg for conventional fuel oils).

The bio-oil formed at 725 K contained high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol, and 2-cyclopenten-1-one, *etc.* A significant characteristic of the bio-oils is the high percentage of alkylated compounds especially methyl derivatives. As the temperature increases, some of these

compounds are transformed *via* hydrolysis. The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways such as dehydration, cyclization, Diels–Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexanedione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% (Demirbas, 2008).

The influence of temperature on the compounds existing in liquid products obtained from biomass samples *via* pyrolysis has been examined in relation to the yield and composition of the product bio-oils. The product liquids were analyzed by a gas chromatography mass spectrometry combined system. The bio-oils were composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaicol, and their alkylated phenol derivatives. Thermal depolymerization and decomposition of biomass structural components, such as cellulose, hemicelluloses, and lignin form liquids and gas products, as well as a solid residue of charcoal. The structural components of the biomass samples mainly affect pyrolytic degradation products. A reaction mechanism is proposed that describes a possible reaction route for the formation of the characteristic compounds found in the oils. The supercritical water extraction and liquefaction partial reactions also occur during the pyrolysis. Acetic acid is formed in the thermal decomposition of all three main components of biomass. In the pyrolysis reactions of biomass water is formed by dehydration, acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit, furfural is formed by dehydration of the xylose unit, formic acid proceeds from carboxylic groups of uronic acid, and methanol arises from methoxyl groups of uronic acid (Demirbas, 2007).

Pyrolysis of wood has been studied as a zonal process with zone A (easily degrading zone) occurring at temperatures up to 475 K. The surface of the wood becomes dehydrates at this temperature, and along with water vapor, carbon dioxide, formic acid, acetic acid, and glyoxal are given off. When temperatures of 475–535 K are attained, the wood is said to be in zone B and is evolving water vapor, carbon dioxide, formic acid, acetic acid, glyoxal, and some carbon monoxide. The reactions to this point are mostly endothermic, the products are largely non-condensable, and the wood is becoming charred. Pyrolysis actually begins between 535 K and 775 K, which is called zone C. The reactions are exothermic, and unless heat is dissipated, the temperature will rise rapidly. Combustible gases such as carbon monoxide from cleaving of carbonyl group, methane, formaldehyde, formic acid, acetic acid, methanol, and hydrogen are being liberated and charcoal is being formed. The primary products are beginning to react with each other before they can escape the reaction zone. If the temperature continues to rise above 775 K, a layer of charcoal will be formed, which is the site of vigorous secondary reactions and is classified as zone D. Carbonization is said to be complete at temperatures of 675 K to 875 K. Thermal degradation properties of hemicelluloses, celluloses, and lignin can be summarized as follows (Demirbas, 2000):

Thermal degradation of hemicelluloses > of cellulose >> of lignin

The liquid fraction of pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics (mainly aromatics) of high molecular weight. This phase is called bio-oil or tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of aqueous phase are higher than those of non-aqueous phase.

If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, and short gas residence time process are required. For a high char production, a low temperature, low heating rate process are chosen. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process should be preferred.

6.6.1 Reaction Mechanism of Pyrolysis

Earlier kinetic studies have been conducted under a variety of experimental conditions, resulting in conflicting data with a wide range of kinetic parameters (Stamm, 1956; Hofmann and Antal, 1984; Desrosiers and Lin, 1984; Demirbas, 1998; Koullas *et al.*, 1998). Thermogravimetric analysis (TGA) is the general approach applied to determine the weight loss of pyrolyzed samples at various reaction temperatures. A comparison of kinetic data from literature is given in Table 6.4.

The pyrolysis process is always initially endothermic, and almost linear in mass loss. At high heating rates, this character is maintained throughout the process. At low heating rates, the well-known exothermic char forming processes at some point begin to complete with the basic endothermic nature of the process, and drive it back towards thermoneutrality. There is, however, no evidence of thermo-

Table 6.4 Comparison of kinetic data from the literature

Biomass	Frequency factor (min^{-1})	Activation energy (kJ/mole)	Temperature range (K)	Researcher
Douglas fir sawdust	1.1×10^{11}	105	368–525	Stamm (1956)
Wood	1.4×10^6	84.2	>605	Barooah and Long (1976)
Douglas fir bark	1.3×10^{10}	100–201	450–850	Tran and Rai (1978)
Missouri oak sawdust	1.5×10^8	106	595–665	Thurner and Mann (1981)
Sawdust	1.9×10^7	95.9	565–665	Koullas <i>et al.</i> (1998)
Hazelnut shell sawdust	4.7×10^{13}	92–170	450–750	Demirbas (1998)

dynamically different pathways being followed at high and low heating rates during the initial stages of pyrolysis. This alone does not assure that a change of mechanism does not occur, but there is also no other evidence to suggest such a change in mechanism with the heating rate.

It is believed that as the pyrolysis reaction progresses the carbon residue (semi-char) becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases (Tran and Charanjit, 1978).

The general changes that occur during pyrolysis are enumerated below (Babu and Chaurasia, 2003; Mohan *et al.*, 2006):

1. Heat transfer from a heat source, to increase the temperature inside the fuel.
2. The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char.
3. The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel.
4. Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar;
5. Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition.
6. Further thermal decomposition, reforming, water gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the residence time/temperature/pressure profile of the process.

A comparison of pyrolysis, ignition, and combustion of coal and biomass particles reveals the following:

1. Pyrolysis starts earlier for biomass as compared with coal.
2. The VM content of biomass is higher compared with that of coal.
3. The fractional heat contribution by VM in biomass is of the order of 70% compared with 36% for coal.
4. Biomass char has more O₂ compared with coal. The fractional heat contribution by biomass is of the order of 30% compared with 70% for coal.
5. The heating value of volatiles is lower for biomass as compared with that of coal.
6. Pyrolysis of biomass chars mostly releases CO, CO₂, and H₂O.
7. Biomass has ash that is more alkaline in nature, which may aggravate fouling problems.

The organic compounds from biomass pyrolysis are the following groups:

1. A gas fraction containing: CO, CO₂, some hydrocarbons and H₂.
2. A condensable fraction containing: H₂O and low molecular weight organic compounds (aldehydes, acids, ketones, and alcohols).
3. A tar fraction containing: higher molecular weight sugar residues, furan derivatives, phenolic compounds and airborne particles of tar and charred material which form smoke.

The mechanism of pyrolysis reactions of biomass has been extensively discussed in an earlier study (Demirbas, 2000). Water is formed by dehydration. In the pyrolysis reactions, methanol arises from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Methanol also arises from methoxyl groups of uronic acid. Acetic acid is formed in the thermal decomposition of all three main components of wood. When the yield of acetic acid originating from the cellulose, hemicelluloses, and lignin is taken into account, the total is considerably less than the yield from the wood itself. Acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit.

In the pyrolysis processes, furfural is formed by dehydration of the xylose unit. Quantitatively, 1-hydroxy-2-propanone and 1-hydroxy-2-butanone present high concentrations in the liquid products. These two alcohols are partly esterified by acetic acid. In conventional slow pyrolysis, these two products are not found in such a great quantity because of their low stability. If wood is completely pyrolyzed, the resulting products are about what would be expected by pyrolyzing the three major components separately. The hemicelluloses would break down first, at temperatures of 470–530 K. Cellulose follows in the temperature range of 510–620 K, with lignin being the last component to pyrolyze at temperatures of 550–770 K. A wide spectrum of organic substances is contained in the pyrolytic liquid fractions given in the literature (Beaumont, 1985). Degradation of xylan yields eight main products: water, methanol, formic, acetic and propionic acids, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, and 2-furfuraldehyde. The methoxy phenol concentration decreased with increasing temperature, while phenols and alkylated phenols increased. The formation of both methoxy phenol and acetic acid was possibly as a result of the Diels–Alder cycloaddition of a conjugated diene and unsaturated furanone or butyrolactone.

Timell (1967) described the chemical structure of the xylan as the 4-methyl-3-acetylglucuronoxylan. It has been reported that the first runs in the pyrolysis of the pyroligneous acid consist of about 50% methanol, 18% acetone, 7% esters, 6% aldehydes, 0.5% ethyl alcohol, 18.5% water, and small amounts of furfural (Demirbas, 2000). Pyroligneous acids disappear in high-temperature pyrolysis.

The composition of the water soluble products was not ascertained but it has been reported to be composed of hydrolysis and oxidation products of glucose such as acetic acid, acetone, simple alcohols, aldehydes, sugars, *etc.* Pyroligneous acids disappear in high-temperature pyrolysis. Levoglucosan is also sensitive to heat and decomposes to acetic acid, acetone, phenols, and water. Methanol arises from the methoxyl groups of uronic acid (Demirbas, 2000).

6.7 Gasification Research and Development

Gasification, one of thermochemical conversion routes, is widely recognized at present because its end product gas can find flexible application by industries or by home users, particularly in decentralized energy production coupled with

microturbine/gas, turbine/engines, boiler, and even fuel cells (Chen *et al.*, 2004). Gasification of biomass is a well-known technology that can be classified depending on the gasifying agent: air, steam, steam-oxygen, air-steam, O₂-enriched air, *etc.*

Gasification describes the process in which oxygen-deficient thermal decomposition of organic matter primarily produces synthesis gas. Gasification is a combination of pyrolysis and combustion. Gasification typically refers to conversion of solid or liquid carbon-based materials by direct internal heating provided by partial oxidation using substoichiometric air or oxygen to produce fuel gases (synthesis gas, producer gas), principally CO, H₂, methane, and lighter hydrocarbons in association with CO₂ and N₂, depending on the process used. Alternative configurations using either indirect heating methods such as externally fired burners, or autothermal methods using exothermic reducing reactions have been demonstrated.

Gasification has more potential for near-term commercial application than other thermochemical processes. Benefits of gasification over combustion include: more flexibility in terms of energy applications, more economical and thermodynamic efficiency at smaller scales, and potentially lower environmental impact when combined with gas cleaning and refining technologies. An efficient gasifier will decompose high-molecular-weight organic compounds released during pyrolysis into low-molecular-weight, non-condensable compounds in a process referred to as tar cracking. Undesirable char that is produced during gasification will participate in a series of endothermic reactions at temperatures above 800°C, which converts carbon into a gaseous fuel. Typically gaseous products include: CO, H₂, and CH₄. Fischer–Tropsch processes may be used to upgrade gaseous products to liquid fuels through the use of catalysts. Gasification requires feedstocks that contain less than 10% moisture.

Gasification is a form of pyrolysis carried out in the presence of a small quantity of oxygen at high temperatures in order to optimize the gas production. The resulting gas, known as the producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. The gas is more versatile than the original solid biomass (usually wood or charcoal); it can be burnt to produce process heat and steam, or used in gas turbines to produce electricity.

Gasification of solids with subsequent combustion of the gasification-derived fuel gases generates the same categories of products as direct combustion of solids, but pollution control and conversion efficiencies may be improved. Alternatively, the produced synthesis gases can be used directly for liquid fuel or chemical synthesis, eliminating or delaying the combustion process, and the emission of the resulting effluent.

Biomass gasification technologies are expected to be an important part of the effort to meet these goals of expanding the use of biomass. Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of biomass electricity generation through the use gas turbine technology. High efficiencies (up to about 50%) are

achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine. Economic studies show that biomass suffocation plants can be as economical as conventional coal-fired plants.

Commercial gasifiers are available in a range of size and types, and run on a variety of fuels, including wood, charcoal, coconut shells, and rice husks. Power output is determined by the economic supply of biomass, which is limited to 80 MW in most regions. The process of synthetic fuels (synfuels) from biomass will lower energy cost, improve waste management, and reduce harmful emissions. This triple assault on plant operating challenges is a proprietary technology that gasifies biomass by reacting it with steam at high temperatures to form a clean burning syngas. The molecules in the biomass (primarily carbon, hydrogen, and oxygen) and the molecules in the steam (hydrogen and oxygen) reorganize to form this syngas.

6.7.1 Biomass Gasification

Biomass gasification technologies have historically been based upon partial oxidation or partial combustion principles, resulting in the production of a hot, dirty, low heating value gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy.

Generating electricity and useful heat from the same power plant is called “cogeneration” in North America and “combined heat and power (CHP)” in Europe. Biomass integrated gasification combined cycle cogeneration technology is not yet commercially available. Gasification is an energy process producing a gas that can substitute fossil fuels in high efficiency power generation, heat and/or cogeneration applications, and can be used for the production of liquid fuels and chemicals *via* synthesis gas.

Biomass gasification has attracted the highest interest amongst the thermochemical conversion technologies as it offers higher efficiencies in relation to combustion, while flash pyrolysis is still in the development stage. The comparison of the environmental impact of biomass use in gasifiers and incinerators is very important when considering the effective use of biomass. However, the high alkali content in biomass can form compounds with low melting temperature during combustion. The low melting ash constituents can induce in-bed-agglomeration, in addition to fouling and corrosion problems.

The energy crisis of the 1970s brought a renewed interest. The technology was perceived as a relatively cheap indigenous alternative for small-scale industrial and utility power generation in those developing countries that suffered from high world market petroleum prices and had sufficient sustainable biomass resources. In the beginning of the 1980s at least ten (mainly European) manufacturers were offering small-scale wood and charcoal fired power plants (up to approximately 250 kW_{el}). At least four developing countries (The Philippines, Brazil, Indonesia, and India)

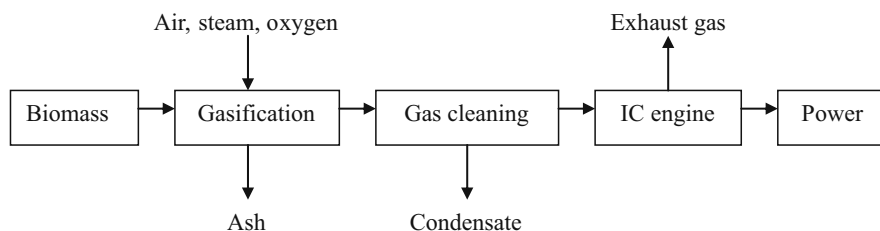


Fig. 6.8 System for power production by means of biomass gasification

started gasifier implementation programs based on locally developed technologies. Figure 6.8 shows the system for power production by means of biomass gasification. The gasification system of biomass in fixed-bed reactors provides the possibility of combined heat and power production in the power range of 100 kWe up to 5 MWe. A system for power production by means of fixed-bed gasification of biomass consists of the main unit gasifier, gas cleaning system, and engine.

The biomass gasification process is similar to processes used for many years by chemical and petrochemical manufacturers, including methanol, ammonia, and ethylene producers. The hydrogen and oxygen molecules in the steam are liberated, and a series of reactions result in a reorganization of the compounds to form synthesis gas (primarily H_2 , CO and CO_2). This synthesis gas is then catalytically converted into methanol, ammonia, or another product.

Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency and to reduce the investment costs of biomass electricity generation through the use gas turbine technology. High efficiencies (up to about 50%) are achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine. Economic studies show that biomass suffocation plants can be as economical as conventional coal-fired plants.

Various gasification technologies include gasifiers where the biomass is introduced at the top of the reactor and the gasifying medium is either directed co-currently (downdraft) or counter-currently up through the packed bed (updraft). Other gasifier designs incorporate circulating or bubbling fluidized beds. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater in the product gases. Table 6.5 shows gasifiers and reactor types using gasification processes.

Table 6.5 Gasifiers and reactor types using gasification processes

Gasifier	Reactor type
Fixed bed	Downdraft, Updraft, Co-current, Counter-current, Cross current, Others
Fluidized bed	Single reactor, Fast fluid bed, Circulating bed
Entrained bed	—
Twin reactor	—
Moving bed	—
Others	—

Table 6.6 Composition of gaseous products from various biomass fuels by different gasification methods (% by volume)

H ₂	CO ₂	O ₂	CH ₄	CO	N ₂
10–19	10–15	0.4–1.5	1–7	15–30	43–60

Commercial gasifiers are available in a range of size and types, and run on a variety of fuels, including wood, charcoal, coconut shells, and rice husks. Power output is determined by the economic supply of biomass, which is limited to 80 MW in most regions. The producer gas is affected by various gasification processes from various biomass feedstocks. Table 6.6 shows the composition of gaseous products from various biomass fuels by different gasification methods.

The relative simplicity of the gasification system enables its operation to be within the technical expertise of most operators experienced with conventional boilers and furnaces, and results in favorable project economics. Its modular design allows a wide range of scale-up or scale-down possibilities, so the systems can vary in size from about 1 ton *per* hour of residue to 20 tons *per* hour or more, with the size being limited only by biomass availability.

6.7.2 Biomass Gasification Systems

The system can gasify a wide variety of biomass wastes and other organic materials generated by many industries. It has gasified, and in most cases has data on expected fuel composition, char analyses, and emissions analyses from the syngas produced for the following feedstocks: hardwood and pine saw dust, bark/hogged fuel, sander/grinder dust from panel board mills, pulp and paper mill sludge, whole and ground rice hulls, sugar cane bagasse, sewage sludge, the cellulosic fraction of municipal solid waste, and several grades of lignite and subbituminous coal.

The main steps in the gasification process are:

- Step 1. Biomass is delivered to a metering bin from which it is conveyed with recycled syngas or steam, without air or oxygen into the gasifier.
- Step 2. The material is reformed into a hot syngas that contains the inorganic (ash) fraction of the biomass and a small amount of unreformed carbon.
- Step 3. The sensible heat in the hot syngas is recovered to produce heat for the reforming process.
- Step 4. The cool syngas passes through a filter and the particulate in the syngas is removed as a dry, innocuous waste. The clean syngas is then available for combustion in engines, turbines, or standard natural gas burners with minor modifications.

The major components of a gasification system are: (a) feed system, (b) primary heat exchanger, (c) primary reformer, (d) gas filter, and (e) final syngas cooler.

Depending upon the size, consistency and nature of the biomass, the material is often routed through a hammer-mill or tub grinder/classifier before entering the plant's metering bin located above the feed system. The material is fed by gravity into the metering bin where it enters a screw feed system. The material is then conveyed through a proprietary sealing mechanism that serves as the pressure seal on the front end of the system, keeping air out of the reformer and keeping syngas from backing up into the feed system. The material received from the screw feeder is then conveyed with recycled compressed syngas into the primary heat exchanger.

The primary heat exchanger serves two functions. First, biomass is conveyed with syngas into the convection section where preheating, devolatilization, and evaporation of water occurs. In addition, after reforming, as the hot syngas leaves the primary reformer, it gives up its sensible heat energy to the primary heat exchanger and is cooled to the desired process temperature before it exits to the gas filter.

The preheated, partially reformed (gasified) biomass and conveying syngas pass from the convection section of the primary heat exchanger into the radiant coil section of the primary reformer where high temperature steam reforming takes place.

This unit receives syngas from the primary heat exchanger. The syngas and any char (inorganic solids and any unreformed carbon) are routed through barrier type filter elements where the char is collected and removed as a dry, innocuous residue. The char is delivered to a collection bin for alternative beneficial reuse or disposal. This air-cooled heat exchanger receives clean syngas from the gas filter and reduces the gas temperature to the desired level for supplying power generation equipment, or other fuel uses.

6.7.2.1 Types of Gasifiers

Numerous types of gasifiers have been developed and tested, and many industrial applications can use the technology. Gasifiers have been built and operated using a wide variety of configurations, including:

1. fixed bed (updraft or downdraft fixed beds) gasifiers,
2. fluidized bed (fluidized or entrained solids serve as the bed material) gasifiers, and
3. others including moving grate beds and molten salt reactors.

Schematic diagrams of updraft (counter current) and downdraft (co-current) fixed bed gasifiers are shown in Figs. 6.9 and 6.10, respectively. Other gasifier designs incorporate circulating or bubbling fluidized beds.

In the drying zone, feedstock descends into the gasifier and moisture is removed using the heat generated in the zones below by evaporation. In the distillation zone, pyrolysis and partial oxidation takes place using the thermal energy released by the partial oxidation of the pyrolysis products. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater in the product gases. The oxidation reactions of the volatiles are very rapid, and the oxygen is consumed before it can diffuse to the surface of the char. In the reduction zone (often referred to as

Fig. 6.9 Schematic diagram of an updraft fixed bed gasifier

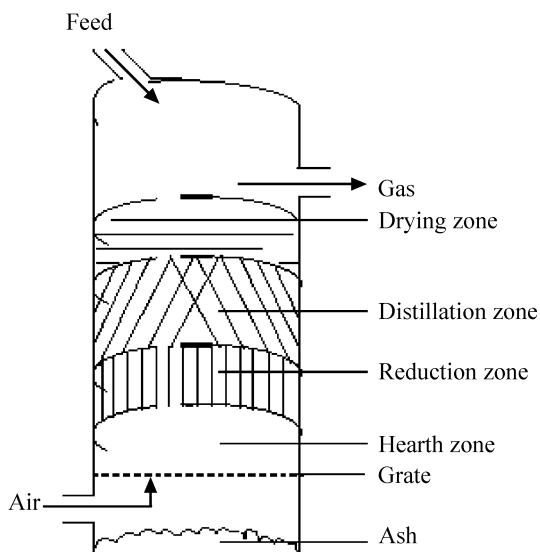
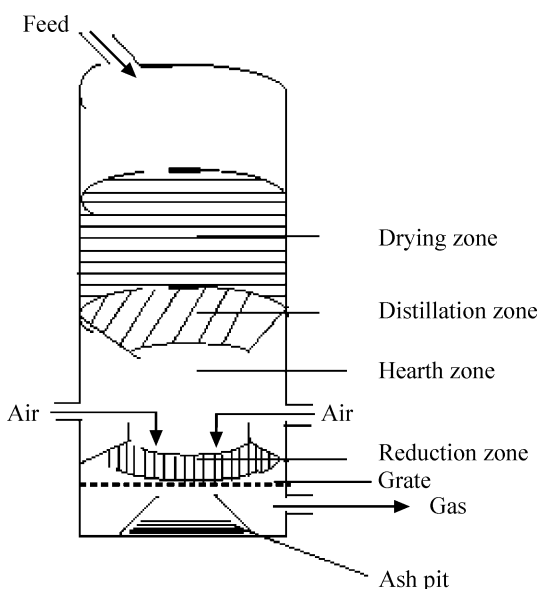


Fig. 6.10 Schematic diagram of a downdraft fixed bed gasifier



the gasification zone) the char is converted into product gas by reaction with the hot gases from the upper zones. Depending in the end use, it is necessary to cool and clean the gas in order to remove as much water vapor, dust, and pyrolytic products as possible from the gas, especially if it is to be used in an internal combustion engine.

Fixed-bed gasifiers are the most suitable for biomass gasification. Fixed-bed gasifiers are usually fed from the top of the reactor and can be designed in either

updraft or downdraft configurations. The product gases from these two gasifier configurations vary significantly. At larger scale, fixed-bed gasifiers can encounter problems with bridging of the biomass feedstock. This leads to uneven gas flow. Achieving uniform temperatures throughout the gasifier at large scale can also be difficult due to the absence of mixing in the reaction zone. Most fixed-bed gasifiers are air-blown and produce low-energy gases (Stevens, 2001).

With fixed-bed updraft gasifiers, the air or oxygen passes upward through a hot reactive zone near the bottom of the gasifier in a direction counter-current to the flow of solid material. Exothermic reactions between air/oxygen and the charcoal in the bed drive the gasification process. Heat in the raw gas is transferred to the biomass feedstock as the hot gases pass upward, and biomass descending through the gasifier sequentially undergoes drying, pyrolysis, and finally gasification. Fixed-bed updraft gasifiers can be scaled up; however, they produce a product gas with very high tar concentrations. This tar should be removed for the major part from the gas, creating a gas-cleaning problem.

Fixed-bed downdraft gasifiers were widely used in World War II for operating vehicles and trucks. During operation, air is drawn downward through a fuel bed; the gas in this case contains relatively less tar compared with the other gasifier types. Fixed-bed downdraft gasifiers are limited in scale and require a well-defined fuel, making them not fuel-flexible.

Fluidized bed (FB) gasifiers are a more recent development that takes advantage of the excellent mixing characteristics and high reaction rates of this method of gas-solid contacting. Examples of FB gasifier systems are the bubbling fluidized bed (BFB) gasifiers, the entrained bed (EB) gasifiers, and the circulating fluidized bed (CFB) gasifiers.

The FB gasifiers are typically operated at 1050–1250 K (limited by the melting properties of the bed material) and are therefore not generally suitable for coal

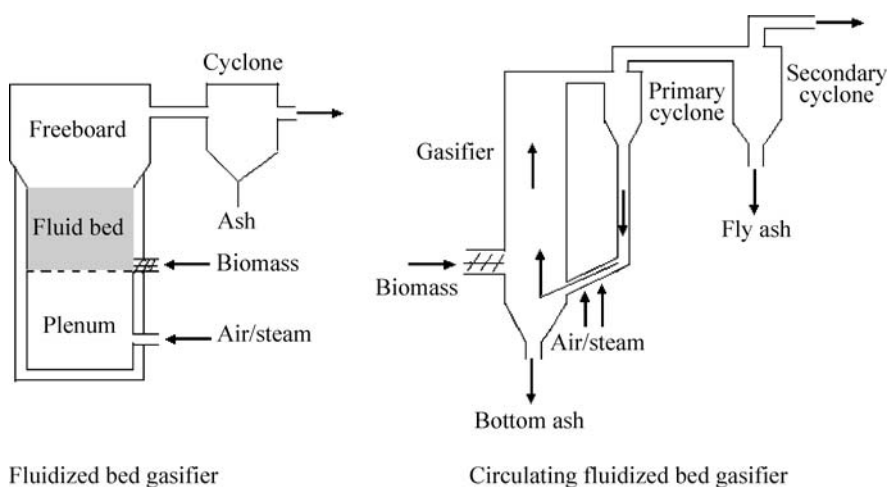
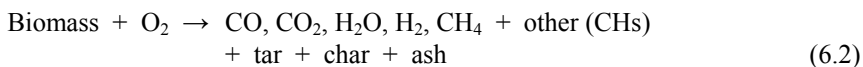


Fig. 6.11 Fluidized bed and circulating fluidized bed gasifier systems

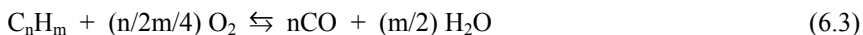
gasification, as due to the lower reactivity of coal compared to biomass, a higher temperature is required ($>1550\text{ K}$). Heat to drive the gasification reaction can be provided in a variety of ways in FB gasifiers. Direct heating occurs when air or oxygen in fluidizing gas partially oxidizes the biomass, and heat is released by the exothermic reactions that occur. Indirect heating methods such as internal heat exchangers, using preheated bed material, or other means can also be used to drive the gasification reactions (Stevens, 2001). The BFB gasifier tends to produce a gas with tar content between that of the updraft and downdraft gasifiers. Some pyrolysis products are swept out of the fluid bed by gasification products, but are then further converted by thermal cracking in the freeboard region (Warnecke, 2000). The CFB gasifiers employ a system where the bed material circulates between the gasifier and a secondary vessel. The CFB gasifiers are suitable for fuel capacity higher than 10 MWth. The FB gasifier and the CFB gasifier systems are shown in Fig 6.11.

6.7.2.2 Short Review of Biomass Gasification Chemistry

Gasification is a complex thermochemical process that consists of a number of elementary chemical reactions, beginning with the partial oxidation of a biomass fuel with a gasifying agent, usually air, oxygen, or steam. The chemical reactions involved in gasification include many reactants and many possible reaction paths. While the reactions that take place in a gasifier are complex, they can be categorized as follows: flash evaporation of inherent moisture, devolatilization of higher organics, heavy hydrocarbon cracking, pyrolysis, and steam reforming. Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. Volatile matter partially oxidizes to yield the combustion products H_2O and CO_2 , plus heat to continue the endothermic gasification process. Yields are product gases from thermal decomposition composed of CO , CO_2 , H_2O , H_2 , CH_4 , other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. Gas composition of the product from the biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition. A generalized reaction describing biomass gasification is as follows:



The relative amount of CO , CO_2 , H_2O , H_2 , and (CHs) depends on the stoichiometry of the gasification process. If air is used as the gasifying agent, then roughly half of the product gas is N_2 . The air/fuel ratio in a gasification process generally ranges from 0.2–0.35 and if steam is the gasifying agent, the steam/biomass ratio is around 1. The actual amount of CO , CO_2 , H_2O , H_2 , tars, and (CHs) depends on the partial oxidation of the volatile products, as shown in Eq. 6.3.



Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. These processes suffer from low thermal efficiencies and low Btu gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy.

In essence, the system embodies a fast, continuous process for pyrolyzing or thermally decomposing biomass and steam reforming the resulting constituents. The entire process occurs in a reducing environment, not an oxidizing environment like other biomass gasifiers. While the reactions that take place in the gasifier are complex, they can be categorized as follows: flash evaporation of inherent moisture, devolatilization of higher organics, heavy hydrocarbon cracking, pyrolysis, and steam reforming. The major thermochemical reactions include the following:

Steam and methane:



Water–gas shift:



Carbon char to methane:



Carbon char oxides (Boudouard reaction):



The process is extremely efficient, achieving over 97% conversion of biomass carbon to useful syngas without producing troublesome tars, oils, or contaminated effluents. The process is also quite robust in its ability to handle feedstocks with varying degrees of inherent moisture, ranging from bone dry wood (in which case moisture is actually added to the feedstock) to organic sludge with moisture contents of over 60%. Unlike traditional partial oxidation systems where any moisture in the feedstock results in an energy efficiency penalty, the process utilizes a portion of the moisture to produce hydrogen and other combustible gases. At 40% moisture in the feedstock, the system achieves a cold gas efficiency of about 80%.

Char gasification is the rate-limiting step in the production of gaseous fuels from biomass. Arrhenius kinetic parameters have been determined for the reaction of chars prepared by pyrolysis of cottonwood at 1275 K with steam and carbon dioxide. Results indicate that both reactions are approximately zero order with respect to char; the overall reaction rate is fairly constant throughout and declines only when the char is nearly depleted. This suggests that the reaction rate depends on such factors as the total available active surface area or the interfacial area between the char and catalyst particles. These parameters would remain relatively constant during the gasification process. Sodium and potassium catalysts were equally effective for the gasification of wood char. The iron and nickel transition metals provided the highest initial catalytic activity, but lost their activ-

ity well before the char completely reacted. Softwood and hardwood chars exhibited similar gasification behavior. Results indicate that the mineral (ash) content and composition of the original biomass material, and pyrolysis conditions under which char is formed significantly influence the char gasification reactivity (Demirbas, 2000).

The char yield in a gasification process can be optimized to maximize carbon conversion or the char can be thermally oxidized to provide heat for the process. Char is partially oxidized or gasified according to the following reactions:



The gasification product gas composition, particularly the H_2 :CO ratio, can be further adjusted by reforming and shift chemistry. Additional hydrogen is formed when CO reacts with excess water vapor according to the water-gas shift reaction given in Eq. 6.5. Carbon chars can be converted to methane according to Eq. 6.6.

6.7.3 Electricity from Cogenerative Biomass Firing Power Plants

Biomass has historically been a dispersed, labor-intensive, and land-intensive source of energy. Biomass provides a clean, renewable energy source that may dramatically improve our environment, economy, and energy security. Biomass energy also creates thousands of jobs and helps revitalize rural communities. Therefore as industrial activity has increased in countries, more concentrated and convenient sources of energy have been substituted for biomass. Biomass accounts for 35% of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption.

In the future, biomass has the potential to provide a cost-effective and sustainable supply of energy, while at the same time aiding countries in meeting their greenhouse gas reduction targets. By the year 2050, it is estimated that 90% of the world population will live in developing countries. It is critical therefore that the biomass processes used in these countries be sustainable. Traditionally, biomass has been utilized through direct combustion, and this process is still widely used in many parts of the world. World production of biomass is estimated at 146 billion metric tons a year, mostly wild plant growth.

The future of biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high-energy conversion efficiencies. Electricity is produced by direct combustion of biomass, advanced gasification and pyrolysis technologies are almost ready for commercial scale use. Biomass power plants (BPPs) use technology that is very similar to that used in coal-fired power plants. For example, biomass plants use similar steam-turbine generators and fuel delivery systems. BPP efficiencies of is about 25%. Electricity costs are in the 6–8 c/kWh range. The average BPP is about 20 MW in size, with a few

dedicated wood-fired plants in the 40–50 MW size range. As the biomass-to-electricity industry grows, it will be characterized by larger facilities of 50–150 MW capacity, with gas turbine/steam combined cycles. Biomass is burned to produce steam, and the steam turns a turbine and drives a generator, producing electricity. Because of potential ash build up, only certain types of biomass materials are used for direct combustion. Heat is used to thermochemically convert biomass into a pyrolysis oil. The oil, which is easier to store and transport than solid biomass material, is then burned like petroleum to generate electricity.

Biomass can be used as a primary energy source or as a secondary energy source to power gas turbines. As a secondary energy source, biomass is used to make a fuel, which can be used to fire a gas turbine. The heat produced from the electricity generating process is captured and utilized to produce domestic purposes and can be used in steam turbines to generate additional electricity. Cogeneration is the simultaneous production of electricity and useful thermal energy from a single source.

One alternative for producing electricity from biomass in a gas turbine is direct combustion of biomass as a primary energy source. Biomass is burned directly to produce steam, the steam turns a turbine, and the turbine drives a generator, producing electricity. Direct combustion usually involves reducing the biomass into fine pieces for fueling a close-coupled turbine system. In a close-coupled system, biomass is burned in a combustion chamber separated from the turbine by a filter.

The pulverized wood fuel can then be burned in a flame in the same way as oil or gas at the same high power output. Burners for coal or peat powder are suitable when adjusted for this proper mixture of fuel and air. Since the same type of boilers and control systems are used, it is easy to combine the different fuels.

Analysis and modeling of combustion in stoves, furnaces, boilers, and industrial processes require adequate knowledge of wood properties. Fuel properties for combustion analysis of wood can be conveniently grouped into physical, thermal, chemical, and mineral properties. Bark properties should be distinguished from wood properties. Thermal degradation products of wood consist of moisture, volatiles, char, and ash. Volatiles are further subdivided into gases and tars. Some properties vary with species, location within the tree, and growth conditions. Other properties depend on the combustion environment. Combustion systems using wood fuel may be generally grouped into fixed bed, suspension burning, and fluidized bed systems. The systems range from residential to commercial and industrial to utility scale. The fuel property data needed depend, of course, on the type of application and the details of the model.

A steam power plant is actually a two-fluid system, that is, energy is exchanged between the combustion gases and water. The feasibility of combining gas and steam expansion in a power cycle has been extensively explored. Because steam generation involves the flow of large volumes of combustion gases, gas expansion is most appropriately accomplished in a gas turbine.

Practically all biomass-based electricity generation plants employ steam turbine systems. Such electricity generation has been established in developed countries in order to upgrade lignocellulosic-based waste materials. Most systems are based on

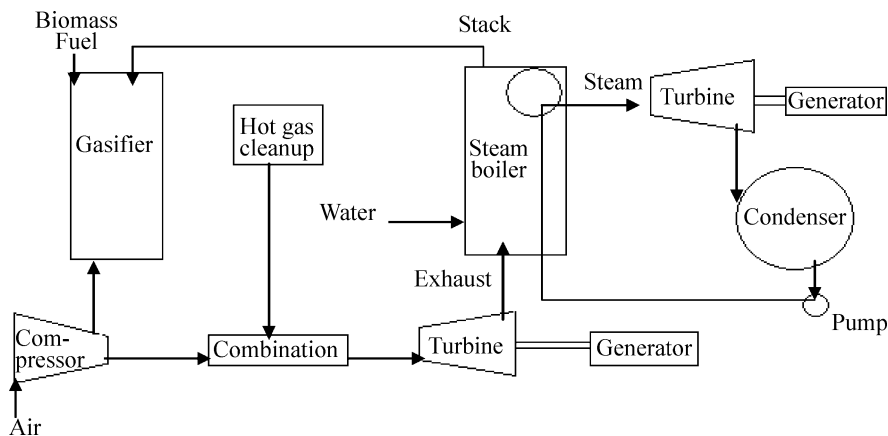


Fig. 6.12 Integrated biomass gas turbine/steam combined cycle power plant

low-pressure boilers (about 20–25 bar) with efficiencies slightly below 20%. Modern biomass powered high pressure (60–100 bar) boiler turbine systems produce electricity with efficiencies approaching 32%. Figure 6.12 shows the integrated biomass gas turbine/steam combined cycle power plant.

How the Gasifier Makes Electricity

1. Wood chips or other biomass materials are loaded into the fuel hopper. The wood handling system removes metal impurities and oversized fuel, and discharges the fuel into the gasifier.
2. Initially, dry wood will be used as fuel, but in later project phases a dryer will be installed to allow wetter fuels to be used. Sand that has been heated to 1275 K is added to the gasifier where the fuel is turned into a gas. The mixture is “fluidized” with steam and enters a cyclone separator.
3. The unburned char and cooled sand is removed and discharged to the combustor.
4. The char is burned by adding combustion air, which heats the sand to 1275 K. The heated sand is removed by the cyclone separator and returned to the gasifier. The fuel gas is cleaned in a scrubber and used to fuel a boiler or gas turbine.

Another alternative is to produce a fuel from biomass as a secondary energy source. Gasifiers are used to convert biomass into a combustible gas (biogas). The biogas is then used to drive a high efficiency, combined cycle gas turbine. Gaseous fuels consist of low-calorific-value and medium-calorific-value gases; the liquid is a primary-pyrolysis oil called biocrude. A number of gasifiers have been developed to produce biogases from biomass and peat. The biogas is then used to drive a high-efficiency, combined-cycle gas turbine.

Heat is used to chemically convert biomass into pyrolysis oil and biocrude. The oil, which is easier to store and transport than solid biomass material, is then

burned like petroleum to generate electricity. Biocrude produced at about 775 K and 1 s residence time and containing water have about the same oxygen and energy content as the original feed. Entrained-flow and fluid-bed pyrolysis processes have been developed.

Gas turbines are used by themselves in a very wide range of applications, most notably for powering aircrafts of all types but also in industrial plants for driving mechanical equipment such as compressors, pumps, and electric generators in electrical utilities, and for producing electric power for peak loads, as well as for intermediate and some base-load duties. The compressor compresses the combustion air to desired pressure (typically 10–25 bar), which reacts with the fuel in the combustor. The hot pressurized flue gases expand in the turbine, which drives the compressor and the additional load (generator). The efficiency of the simple cycle gas turbine can be increased by recovering some heat of the exhaust gases by heating the compressed combustion air. An increase in efficiency of 30% is possible.

In a combined cycle, the heat contained in the exiting flue gases from a gas turbine without heat recovery can be used to produce steam. This steam can either be injected in the turbine of the gas turbine, the so-called steam injected gas turbine, or in a separate steam turbine in a so-called steam and gas turbine.

6.7.4 Fischer–Tropsch Synthesis (FTS)

FTS is a well established process for the production of synfuels. The process is used commercially in South Africa by Sasol and Mossgas, and in Malaysia by Shell. FTS can be operated at low temperatures (LTFT) to produce a syncrude with a large fraction of heavy, waxy hydrocarbons or it can be operated at higher temperatures (HTFT) to produce a light syncrude and olefins. With HTFT the primary products can be refined to environmentally friendly gasoline and diesel, solvents, and olefins. With LTFT, the heavy hydrocarbons can be refined to specialty waxes, or if hydrocracked and/or isomerized, to produce excellent diesel, base stock for lube oils, and a naphtha that is ideal feedstock for cracking to light olefins.

FTS has been widely investigated for more than 70 years, and Fe and Co are typical catalysts. Cobalt-based catalysts are preferred because their productivity is better than Fe due to their high activity, selectivity for linear hydrocarbons, and low activity for the competing water–gas shift reaction.

The variety of composition of FT products with hundreds of individual compounds shows a remarkable degree of order with regard to class and size of the molecules. Starting from the concept of FTS as an ideal polymerization reaction, it is easily realized that the main primary products, olefins, can undergo secondary reactions and thereby modify the product distribution. This generally leads to chain length dependencies of certain olefin reaction possibilities, which are again suited to serve as a characteristic feature for the kind of olefin conversion.

Table 6.7 Typical composition of syngas

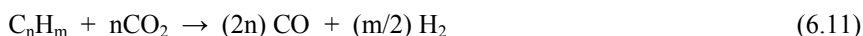
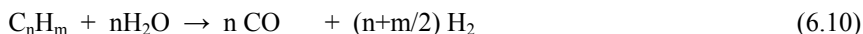
Gas	% by volume
Hydrogen	29–40
Carbon monoxide	21–32
Methane	10–15
Carbon dioxide	15–20
Ethylene	0.4–1.2
Water vapor	4–8
Nitrogen	0.6–1.2

While gasification processes vary considerably, typically gasifiers operate from 975 K and higher and from atmospheric pressure to 5 atm or higher. The process is generally optimized to produce fuel or feedstock gases. Gasification processes also produce a solid residue such as a char, ash, or slag. The product fuel gases, including hydrogen, can be used in internal and external combustion engines, fuel cells, and other prime movers for heat and mechanical or electrical power. Gasification products can be used to produce methanol, FT liquids, and other fuel liquids and chemicals. The typical composition of the syngas is given in Table 6.7.

In all types of gasification, biomass is thermochemically converted to a low or medium-energy content gas. The higher heating value of syngas produced from biomass in the gasifier is typically 10–13 MJ/Nm³. Air-blown biomass gasification results in approximately 5 MJ/Nm³ and oxygen-blown 15 MJ/Nm³ of gas and is considered a low to medium energy content gas compared to natural gas (35 MJ/Nm³).

The process of synfuels from biomass will lower energy costs, improve the waste management, and reduce harmful emissions. This triple assault on plant operating challenges is a proprietary technology that gasifies biomass by reacting it with steam at high temperatures to form a clean burning syngas. The molecules in the biomass (primarily carbon, hydrogen and oxygen), and the molecules in the steam (hydrogen and oxygen) reorganize to form this syngas.

Reforming the light hydrocarbons and tars formed during biomass gasification also produces hydrogen. In essence, the system embodies a fast, continuous process for pyrolyzing or thermally decomposing biomass and steam reforming the resulting constituents. The entire process occurs in biomass gasifiers by reforming the light hydrocarbons (C₂H₆–C₅H₁₂). Reforming the light hydrocarbons and tars formed during biomass gasification also produces hydrogen. Steam reforming and so-called dry or CO₂ reforming occur according to the following reactions and are usually promoted by the use of catalysts:



The high-temperature FT technology applied by Sasol in the Synthol process in South Africa at the Secunda petrochemical site is the largest commercial scale

application of FT technology. The most recent version of this technology is the Sasol Advanced Synthol (SAS) process. Although FTS was initially envisioned as a means to make transportation fuels, there has been a growing realization that the profitability of commercial operations can be improved by the production of chemicals or chemical feedstock. FTS yields a complex mixture of saturated or unsaturated hydrocarbons (C_1 – C_{40+}), C_1 – C_{16+} oxygenates as well as water and CO_2 . Laboratory studies are often carried out in differential conditions (conversions of approx. 3%) and therefore very accurate product analysis is necessary. Hydrocarbons obtained from a SAS type reactor are: for C_5 – C_{10} and C_{11} – C_{14} hydrocarbons; paraffins 13% and 15%, olefins 70% and 60%, aromatics 5% and 15%, and oxygenates 12% and 10%, respectively. From the component breakdown of the main liquid cuts it is clear that there is considerable scope for producing chemical products in addition to hydrocarbon fuels.

FTS in the supercritical phase can be developed, and its reaction behavior and mass transfer phenomenon have been analyzed by both experimental and simulation methods. The same reaction apparatus and catalysts can be used for both gas phase reaction and liquid phase FT reactions to correctly compare characteristic features of diffusion dynamics and the reaction itself, in various reaction phases. Efficient transportation of reactants and products to the inside of catalysts bed and pellet, quick heat transfer, and *in situ* product extraction from catalysts by supercritical fluid can be accomplished.

There has been an increasing interest in the effect of water on cobalt FT catalysts in recent years. Water is produced in large amounts over cobalt catalysts since one water molecule is produced for each C-atom added to a growing hydrocarbon chain and due to the low water-gas-shift activity of cobalt. The presence of water during FTS may affect the synthesis rate reversibly as reported for titania-supported catalysts, the deactivation rate as reported for alumina-supported catalysts, and water also has a significant effect on the selectivity of cobalt catalysts on different supports. The effect on the rate and the deactivation appears to depend on the catalyst system studied, while the main trends in the effect on selectivity appear to be more consistent for different supported cobalt systems. There are, however, also some differences in the selectivity effects observed. The present study deals mainly with the effect of water on the selectivity of alumina-supported cobalt catalysts, but some data on the activity change will also be reported. The results will be compared with results for other supported cobalt systems reported in the literature.

The activity and selectivity of supported Co FTS catalysts depends on both the number of Co surface atoms and on their density within support particles, as well as on transport limitations that restrict access to these sites. Catalyst preparation variables available to modify these properties include cobalt precursor type and loading level, support composition and structure, pretreatment procedures, and the presence of promoters or additives. Secondary reactions can strongly influence product selectivity. For example, the presence of acid sites can lead to the useful formation of branched paraffins directly during the FTS step. However, product water not only oxidizes Co sites making them inactive for additional turnovers, but

it can inhibit secondary isomerization reactions on any acid sites intentionally placed in FTS reactors.

The iron catalysts used commercially by Sasol in the Fischer–Tropsch synthesis for the past five decades (Dry, 1981) have several advantages: (1) lower cost relative to cobalt and ruthenium catalysts, (2) high water–gas-shift activity allowing utilization of syngas feeds of relatively low hydrogen content such as those produced by gasification of coal and biomass, (3) relatively high activity for production of liquid and waxy hydrocarbons readily refined to gasoline and diesel fuels, and (4) high selectivity for olefinic C_2 – C_6 hydrocarbons used as chemical feedstocks. The typical catalyst used in fixed bed reactors is an unsupported Fe/Cu/K catalyst prepared by precipitation. While having the previously-mentioned advantages, this catalyst (1) deactivates irreversibly over a period of months to a few years by sintering, oxidation, formation of inactive surface carbons, and transformation of active carbide phases to inactive carbide phases, and (2) undergoes attrition at unacceptably high rates in the otherwise highly-efficient, economical slurry bubble-column reactor. Attempts to understand and correct these problems have been impeded by the complexities of oxide and carbide phases and their transformations during pretreatment and reaction. However, it is clear from these previous efforts that the deactivation processes are an inherent consequence of unsophisticated preparation and pretreatment methods developed by trial and error without regard to a rational design of active, stable phases at the nanoscale.

It is well known that addition of alkali to iron causes an increase of both the 1-alkene selectivity and the average carbon number of produced hydrocarbons. While the promoter effects on iron has been thoroughly studied only few and at a first glance contradictory results are available for cobalt catalysts. In order to complete experimental data the carbon number distributions have been analyzed for products obtained in a fixed bed reactor under the steady state condition. Precipitated iron and cobalt catalysts with and without K_2CO_3 were used.

Activated carbon (AC) is a high surface area support with a very unique property that its textural and surface chemical properties can be changed by an easy treatment like oxidation, and these changes affect the properties of the resultant catalysts prepared with AC.

6.7.5 *Supercritical Steam Gasification*

Recently, the supercritical fluid treatment has been considered to be an attractive alternative in science and technology as a chemical reaction field. The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. In addition, ionic product and dielectric constant of supercritical water are important parameters for chemical reaction. Therefore, the supercritical water can be realized from the ionic reaction field to the radical reaction field. For example, ionic product of the supercritical water can be increased by increasing pressure then the hydrolysis reaction field is realized. Therefore, the supercritical

water is expected to be used as a solvent for converting biomass into valuable substances.

The reforming in supercritical water (SCW) offers several advantages over the conventional technologies because of the unusual properties of supercritical water. The density of supercritical water is higher than that of steam, which results in a high space–time yield. The higher thermal conductivity and specific heat of supercritical water is beneficial for carrying out the endothermic reforming reactions. In the supercritical region, the dielectric constant of water is much lower. Further, the number of hydrogen bonds is much smaller and their strength is considerably weaker. As a result, SCW behaves as an organic solvent and exhibits extraordinary solubility toward organic compounds containing large non-polar groups and most permanent gases. Another advantage of SCW reforming is that the H_2 is produced at a high pressure, which can be stored directly, thus avoiding the large energy expenditures associated with its compression. The SCWG process becomes economical as the compression work is reduced owing to the low compressibility of liquid feed when compared to that of gaseous H_2 . Figure 6.13 shows the schematic set-up of the system for supercritical water liquefaction of biomass.

In supercritical water gasification, the reaction generally takes place at the temperature over 875 K and a pressure higher than the critical point of water. With temperature higher than 875 K, water becomes a strong oxidant, and oxygen in water can be transferred to the carbon atoms of the biomass. As a result of the high density, carbon is preferentially oxidized into CO_2 but also low concentrations of

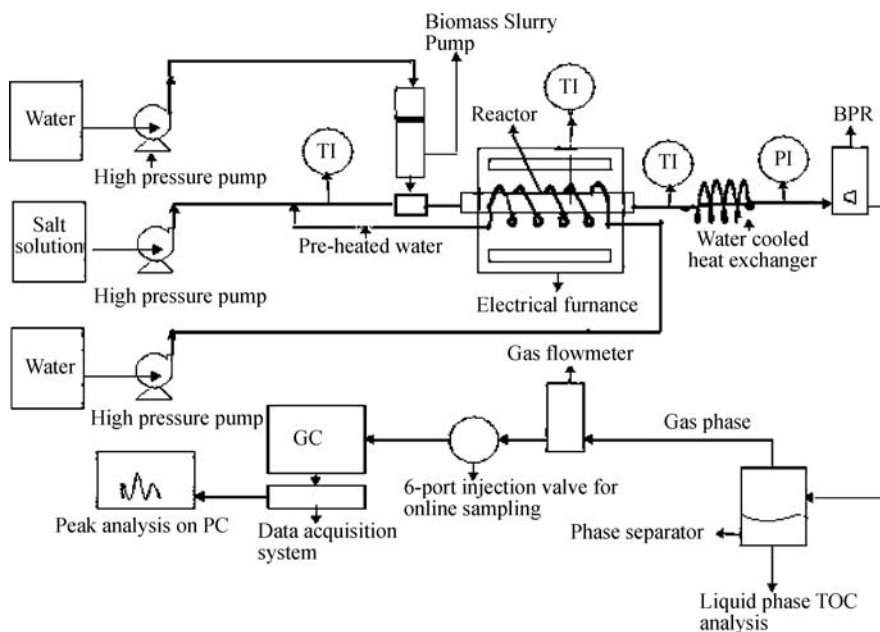


Fig. 6.13 Schematic set-up of the system for supercritical water gasification and liquefaction of biomass

CO are formed. The hydrogen atoms of water and of the biomass are set free and form H_2 . The gas product consists of hydrogen, CO_2 , CH_4 , and CO.

A problem of general nature in SCWG is the required heat exchange between the reactor outlet and inlet streams. To achieve an acceptable thermal efficiency, it is crucial for the process that the heat of the inlet stream is utilized as far as possible to preheat the feedstock stream (mainly water) to reaction conditions. At the same time, heating of the biomass slurry in the inlet tube of a reactor is likely to cause fouling/plugging problems because the thermal decomposition ($>525\text{ K}$) starts already far below the desired reaction temperature ($>875\text{ K}$) (Gadhe and Gupta, 2007). In addition to being a high mass transfer effect, supercritical water also participates in the reforming reaction. The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. Therefore, it is expected that the chemical reactivity can be high in it. In addition, the ionic product and dielectric constant of supercritical water, which are important parameters for chemical reactions, can be continuously controlled by regulating pressure and temperature. Pressure has a negligible effect on hydrogen yield above the critical pressure of water. As the temperature is increased from 600°C to 800°C the H_2 yield increases from 53% to 73% by volume, respectively. Only a small amount of hydrogen is formed at low temperatures, indicating that direct reformation reaction of ethanol as a model compound in SCW is favored at high temperatures ($>700^\circ\text{C}$). With an increase in the temperature, the hydrogen and carbon dioxide yields increase, while the methane yield decreases. The water excess leads to a preference for the formation of hydrogen and carbon dioxide instead of carbon monoxide. The formed intermediate carbon monoxide reacts with water to hydrogen and carbon dioxide. The low carbon monoxide yield indicates that the water-gas-shift reaction approaches completion (Byrd *et al.*, 2007).

Thermochemical gasification of biomass has been identified as a possible system to produce renewable hydrogen with less dependence on exhaustible fossil energy resources. Compared with other biomass thermochemical gasifications, such as air gasification or steam gasification, SCWG has high gasification efficiency at lower temperature and can deal directly with wet biomass without drying.

The capillaries (1 mm ID and 150 mm length tubular reactors) are heated rapidly (within 5 s) in a fluidized sand bed to the desired reaction temperature. Experimentation with the batch capillary method has revealed that, especially at low temperatures and high feed concentrations, char formation occurs. A fluidized bed reactor might be a good alternative to solve the problems related to this char and ash formation.

Cellulose and sawdust were gasified in supercritical water to produce hydrogen-rich gas, and Ru/C, Pd/C, CeO_2 particles, nano- CeO_2 and nano- $(CeZr)_xO_2$ were selected as catalysts. The experimental results showed that the catalytic activities were $Ru/C > Pd/C > nano-(CeZr)_xO_2 > nano-CeO_2 > CeO_2$ particle in turn. The 10 wt% cellulose or sawdust with CMC can be gasified near completely with Ru/C catalyst to produce 2–4 g hydrogen yield and 11–15 g potential hydrogen yield *per* 100 g feedstock at the condition of 773 K, 27 MPa, 20 min residence time in supercritical water (Hao *et al.*, 2005).

Catalysts for low-temperature gasification include combinations of stable metals, such as ruthenium or nickel bimetallics and stable supports, such as certain titania, zirconia, or carbon. Without catalyst the gasification is limited (Kruse *et al.*, 2000). Sodium carbonate is effective in increasing the gasification efficiency of cellulose (Minowa *et al.*, 1997). Likewise, homogeneous, alkali catalysts have been employed for high-temperature supercritical water gasification.

Hydrogen is a sustainable, non-polluting source of energy that can be used in mobile and stationary applications. In order to evaluate hydrogen production by SCWG of various types of biomass, extensive experimental investigations have been conducted in recent years. The supercritical water reforming of biomass materials has been found to be an effective technique for the production of hydrogen with short residence times. Hydrogen production by biomass SCW is a promising technology for utilizing high moisture content biomass.

The product gases mainly consisted of hydrogen and carbon dioxide, with a small amount of methane and carbon monoxide in SCW reforming. Hydrogen yields approaching the stoichiometric limit were obtained under catalytic supercritical water conditions. Hydrogen production is influenced by temperature, residence time, and biomass concentration. The high yield of hydrogen was obtained at high reactor temperature, low residence time, and low biomass concentration. The gas product from biomass gasification in catalytic supercritical water contains about 69% H₂ and 30% CO₂ in mole fraction. Others like CH₄ and CO exist in the gas product in less amounts.

Since a drying process is an energy-intensive operation, and the produced H₂ will be stored under high pressure, supercritical water gasification is a promising technology for gasifying biomass with high moisture content.

References

- Appel, H.R., Fu, Y.C., Friedman, S., Yavorsky, P.M., Wender, I. 1971. Converting organic wastes to oil. US Bureau of Mines Report of Investigation. No. 7560.
- Appell, H., Fu, Y., Friedman, S., Yavorsky, P., Wender, I. 1980. Converting organic wastes to oil: A replenishable energy source. Washington, D.C. Bureau of Mines, U.S. Department of the Interior.
- Babu, B.V., Chaurasia, A.S. 2003. Modeling for pyrolysis of solid particle: Kinetics and heat transfer effects. *Energy Convers Mgmt* 44:2251–2275.
- Byrd, A.J., Pant, K.K., Gupta, R.B. 2007. Hydrogen production from glucose using Ru/Al₂O₃ catalyst in supercritical water. *Ind Eng Chem Res* 46:3574–3579.
- Balat, M. 2008. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources, Part A* 30:620–625.
- Beaumont, O. 1985. Flash pyrolysis products from beech wood. *Wood Fiber Sci.* 17:228–239.
- Barooah, J.N., Long, V.D. 1976. Rates of thermal decomposition of some carbonaceous materials in a fluidized bed. *Fuel* 55:116–120.
- Chen, G., Spliethoff, H., Andries, J., Glazer, M.P., Yang, L.B. 2004 Biomass gasification in acirculating fluidised bed-Part I: Preliminary experiments and modeling development. *Energy Sources* 26:485–498.

- Chornet, E., Overend, R.P. 1985. Fundamentals of thermochemical biomass conversion, pp. 967–1002. Elsevier, New York.
- Datta, B., McAuliffe, C. 1993. The production of fuels by cellulose liquefaction. In Proceedings of First Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry. Golden, CO: National Renewable Energy Laboratory. 931–946.
- Demirbas, A. 1985. A new method on wood liquefaction. *Chim. Acta Turc* 13:363–368.
- Demirbas, A. 1998. Kinetics for non-isothermal flash pyrolysis of hazelnut shell. *Bioresource Technol* 66:247–252.
- Demirbas, A. 2000. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Mgmt* 41:633–646.
- Demirbas, A. 2007. The influence of temperature on the yields of compounds existing in bio-oils obtaining from biomass samples via pyrolysis. *Fuel Proc Technol* 88:591–597.
- Demirbas, A. 2008. The Importance of bioethanol and biodiesel from biomass. *Energy Sources Part B* 3:177–185.
- Desrosiers, R.E., Lin, R.J. 1984. A moving-boundary model of biomass pyrolysis. *Solar Energy* 33:187–196.
- Dry, M.E. 1981. The Fischer–Tropsch synthesis. In Anderson, J.R., Boudart, M. (eds.) *Catalysis: Science and Technology*, Vol. 1, p. 160. Springer, New York.
- Eager, R.L., Mathews, J.F., Pepper, J.M. 1982. Liquefaction of aspen poplar wood. *Canadian J Chem Eng* 60:289–94.
- Feng, W., van der Kooi, H.J., Arons, J.D.S. 2004. Biomass conversions in subcritical and supercritical water: driving force, phase equilibria, and thermodynamic analysis. *Chem Eng Proc* 43:1459–1467.
- Gadhe, J.B., Gupta, R.B. 2007. Hydrogen production by methanol reforming in supercritical water: Catalysis by *in-situ*-generated copper nanoparticles. *Int J Hydrogen Energy* 2007;32:2374–2381.
- Goudriaan, F., Peferoen, D. 1990. Liquid fuels from biomass *via* a hydrothermal process. *Chem Eng Sci* 45:2729–2734.
- Hao, H., Guo, L., Zhang, X., Guan, Y. 2005. Hydrogen production from catalytic gasification of cellulose in supercritical water. *Chem Eng J* 110:57–65.
- He, W., Li, G., Kong, L., Wang, H., Huang, J., Xu, J. 2008. Application of hydrothermal reaction in resource recovery of organic wastes. *Res Conserv Recyc* 52:691–699.
- Hofmann, L., Antal, M.J., Jr. 1984. Numerical simulations of the performance of solar fired flash pyrolysis reactors. *Solar Energy* 33:427–440.
- Inoue, S., Sawayma, S., Dote, Y., Ogi, T. 1997. Behavior of nitrogen during liquefaction of dewatered sewage sludge. *Biomass Bioenergy* 12:473–475.
- Itoh, S., Suzuki, A., Nakamura, T., Yokoyama, S. 1994. Production of heavy oil from sewage sludge by direct thermochemical liquefaction. Proceedings of the IDA and WRPC World Conference on Desalination and Water Treatment. 98:127–133.
- Jomaa, S. 2001. Combined sludge treatment and production of useful organic byproducts using hydrothermal oxidation. PhD thesis. Brisbane, Australia: Department of Civil Engineering, Queensland University of Technology.
- Jomaa, S., Shanableh, A., Khalil, W., and Trebilco, B. 2003. Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products. *Adv Environ Res* 7:647–53.
- Koullas, D.P., Nikolaou, N., Koukkios, E.G. 1998. Modelling non-isothermal kinetics of biomass prepyrolysis at low pressure. *Bioresource Technol* 63:261–266.
- Kranich, W.L. 1984. Conversion of sewage sludge to oil by hydrol liquefaction. EPA-600/2-84-010. Report for the U.S. Environmental Protection Agency. Cincinnati, OH. EPA.
- Kruse, A., Meier, D., Rimbrecht, P., Schacht, M. 2000. Gasification of pyrocatechol in supercritical water in the presence of potassium hydroxide. *Ind Eng Chem Res* 39:2842–2848.
- Minowa, T., Ogi, T., Dote, Y., Yokoyama, S. 1994. Effect of lignin content on direct liquefaction of bark. *Int Chem Eng* 34:428–30.

- Minowa, T., Zhen, F., Ogi, T. 1997. Cellulose decomposition in hot-compressed water with alkali or nickel catalyst. *J Supercritical Fluids* 13:253–259.
- Mohan, D., Pittman Jr., C.U., Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* 2006;20:848–889.
- Molten, P.M., Demmitt, T.F., Donovan, J M., Miller, R.K. 1983. Mechanism of conversion of cellulose wastes to liquid in alkaline solution. In Klass, D.L. (ed.). *Energy from biomass and wastes III*. Chicago, IL: Institute of Gas Technology, p. 293.
- Ogi, T., Yokoyama, S.D. 1993. Liquid fuel production from woody biomass by direct liquefaction. *Sekiyu Gakkaishi* 36:73–84.
- Ogi, T., Yokoyama, S., Koguchi, K. 1985. Direct liquefaction of wood by alkali and alkaline earth salt in an aqueous phase. *Chemical Letters* 8:1199–200.
- Shanableh, A., Jomaa, S. 1998. A versatile supercritical water oxidation system for hazardous Organic waste destruction. In: *Fourth national hazardous and solid waste convention*, CD Rom record no. 1/90, Brisbane, Australia.
- Stamm, A.J. 1956. Thermal degradation of wood and cellulose. *Ind Engng Chem* 48:413–417.
- Stevens, D.J. 2001. Hot gas conditioning: Recent progress with larger-scale biomass gasification systems. National Renewable Energy Laboratory, NREL/SR-510-29952, 1617 Cole Boulevard, Golden, CO.
- Suzuki, A., Yokoyama, S., Murakami, M., Ogi, T., and Koguchi, K. New treatment of sewage sludge by direct thermochemical liquefaction. *Chemistry Letters CMLTAG.I* 9:1425–1428.
- Tester, J. W., Cline, J. A. 1999. Hydrolysis and oxidation in sub-critical and supercritical water: connecting process engineering science to molecular interactions. *Corrosion* 55:1088–100.
- Timell, T.E. 1967. Recent progress in the chemistry of wood. *Hemicelluloses. Wood Sci Technol* 1:45–70.
- Tran, D.Q., Charanjit, R. 1978. A kinetic model for pyrolysis of Douglas fir bark. *Fuel* 57:293–298.
- Zhong, Z., Peters, C. J., de Swaan Arons, J. 2002. Thermodynamic modeling of biomass conversion processes. *Fluid Phase Equilibria* 194–197:805–815.
- Warnecke, R. 2000. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. *Biomass Bioenergy* 18:489–497.